SCATTERING OF HYDRIDE IONS
IN OXYGEN GAS

By

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John Murray McGuire

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CHAPTER I

NEGATIVE IONS

The existence of negative ions was postulated for solutions in the early days of electrolytic theories of conductance. Consideration of equilibrium phenomena such as precipitations in solutions has long demonstrated, as has electrolysis of solutions, the existence of negatively charged particles, other than electrons, in solution. The term "particles" is used in preference to "ions" due to the presence, in general, of solvated clusters in solution rather than simple ions.

Studies of the crystal diffraction of X-rays have also established that many crystals are ionic in their structure and consist of free ions held together by electro-static forces. It was later shown that the particles which carried negative electricity in gaseous discharges were not restricted to electrons; thus negative ions were shown to exist in the gaseous state.

As might be expected, certain ions which have been postulated as organic intermediates have been found by mass spectrometric means while others have not. In cases where the postulated intermediate is actually confirmed by mass spectrometric data, its existence may
generally be regarded as having been established as a free ion. However, this does not mean that it exists in any other form. A number of ions, postulated in mechanisms, have been reported by this method; e.g., $O^-$, $NO_2^-$, $NO_3^-$ (1), $OH^-$, $Li^-$ (2), and $C_2H^-$ (3).

Many of the elements have been shown to have a tendency to form negative ions, the tendency increasing with increasing electron affinity. The rare gases are noteworthy in that there are apparently no stable negative ions formed. This has been attributed to the necessity for the added electron having a higher quantum number than the outer atomic electrons, due to the Pauli exclusion principle.

The hydride ion has been the subject of a number of calculations due to its relative simplicity. It has been shown by Hylleraas (4) that while the undisturbed state of the atom is not sufficient to produce stability, the strong interaction in the $1s$ state rearranges the charge distribution enough to cause stability in the resultant ion. The presence of this ion in the solar spectrum has now been definitely established (5).

In brief, negative ions are known to exist in all physical states. They are stable in the solid state due to electro-static equilibrium (as in ionic crystals). In the liquid or gaseous state they will migrate under the influence of applied potentials (as in electrolysis of solutions). In the gaseous state, they may be produced by such diverse means as natural processes in the upper atmosphere or, in the laboratory,
by thermal dissociation of ionic salts.

The general equations for negative ion production may be written down:

\[(1.1)\] \(A^+ B^- = A^+ + B^-\)

\[(1.2)\] \(AB + C^- = AC + B^-\)

\[(1.3)\] \(A + e + M = A^- + M\)

\[(1.4)\] \(A_2 + e = A^- + A\)

\[(1.5)\] \(A + e = A^- + h\nu\)

\[(1.6)\] \(A + B^- = A^- + B\)

\[(1.7)\] \(A + B^- = AB^-\)

\[(1.8)\] \(A^+ + S = A^- + S^{++}\)

\[(1.9)\] \(AB + e = A^- + B^+ + e\)

Equation (1.1) represents the dissociation of two ions held by electrostatic forces; this process occurs on solution of an ionic salt or upon the very strong heating of one. Equation (1.2) may be illustrated by the ion exchange process in solution. In equation (1.3), M represents any atom which serves to stabilize the negative ion by removing excess
energy. Dissociative attachment by electron collision is represented by equation (1.4). Equation (1.5) is an example of radiative attachment by an atom of an electron with simultaneous emission of a photon. (1.6) is an important equation demonstrating charge exchange between a negative ion and a neutral atom. This process has been reported by Dukelskii and Zandberg (6). In equation (1.7) the formation of an excited negative molecular ion from collision of an atom and a negative ion is illustrated. Equation (1.8) represents negative ion formation by reflection of a positive ion from a metal surface.

Negative ion destruction may proceed according to one of the following equations:

\begin{align}
(1.10) \quad A^- + B &= A + B + e \\
(1.11) \quad A^- + B &= A + B^- \\
(1.12) \quad A^- + B &= AB + e \\
(1.13) \quad A^- + S &= A + S^- \\
(1.14) \quad A^- + B^+ &= AB + h\nu \\
(1.15) \quad A^- + B^+ &= A^* + B^* \\
(1.16) \quad A^- + B^+ + M &= AB + M
\end{align}
(1.17) \( A^- + e = A + 2e \)

(1.18) \( A^- + h\nu = A + e \)

(1.19) \( A^- + B^* = A + B + e \)

The symbols, \( S \) and \( M \), used in equations (1.10-1.19) have the same meaning as in equations (1.1-1.9). In low velocity scattering, the two most important destructive processes are illustrated by equations (1.10) and (1.11): the first shows electron detachment from a negative ion by collision with an atom; the second, shows charge exchange between the ion and the atom.
CHAPTER II

SCATTERING

Simple scattering theory is based on four assumptions: first, the system is a conservative one; second, the scattering particle may be considered initially at rest with respect to the scattered particle; third, that the force field is a central one; and, a non-essential assumption to simplify the treatment, that the scattering angle is small. Since the analysis, based on this last assumption, gives results within the experimental error of an exact treatment (7, 8), it appears to be a justifiable assumption. The application of this theory to the problem of this dissertation is given in Chapter V.

Scattering of beams is a powerful tool which has been used for different purposes in a number of cases. In one of the most simple experimental forms, it has been used to determine the equivalent wave length of electrons (9). In recent years, it has been used for such seemingly diverse purposes as determining the force law between relatively high velocity atoms and molecules (10) and measuring electron exchange cross-sections (11, 12).
Scattering is also applied in determination of nuclear structure, and has been so used over a wide range of elements. The nucleus to be studied is bombarded by a particular type of particle (e.g., alpha particles or neutrons) and, through determination of the scattering behavior, conclusions are drawn as to the structure of the nucleus itself.

The scattering of atoms by gases is similar in principle to the present work; however, the great difficulties encountered in measuring the intensities of neutral scattered particles have restricted the measurements to considerably higher energies than those used in the determination of low velocity ion interaction with gases.

The investigation of elastic scattering of low velocity ions may be said to originate with the work of Russell, Fontana, and Simons (13) in 1941. This paper did not make provision for the quantitative separation of inelastic scattering from elastic scattering and, consequently, the results were less definite than later experimental work based on the apparatus described by Simons, Francis, Fontana, and Jackson (14). Results obtained in these experiments cover the scattering of $\text{H}^+$, $\text{H}_2^+$, and $\text{H}_3^+$ ions in a variety of gases. The potential laws operating over a given energy range between the ion and the scattering particles have been evaluated. In many cases the nature of the interaction may be deduced from the potential law. Naturally, this technique presents an unambiguous method for determining proton affinities and has been used
for such a purpose (13).

The field of negative ion scattering is one in which little work has been done (16). With the exception of the negative ion source, the apparatus used in this dissertation was similar to that used by Simons and co-workers (8, 12, 14, 15) in the study of positive ion scattering.

Since the low velocity scattering of positive ions in gases has contributed useful information as to ion-molecule interactions, it was felt that the same type of experiments with negative ions would also yield useful results. This view was strengthened by the present lack of definite knowledge in the field of negative ions. In the light of these acts, the research for this dissertation was undertaken in order to contribute to the understanding of the laws governing such behavior.
CHAPTER III

DESCRIPTION OF APPARATUS

The apparatus used for the scattering measurements was essentially the same as that described by Muschliitz, Bailey and Simons (16) in Technical report #2 to the Office of Naval Research under contract Nonr 580(01) with several minor changes.

This apparatus utilizes electro-static focusing combined with magnetic field selection of the desired negative ions. The ions, produced by collisions of gas molecules with an electron stream, are collimated into a well-defined pencil by empirical focusing of electro-static elements concentric with the desired pencil. The beam then passes through a magnetic chamber where a particular charge-to-mass ratio may be selected by varying the magnetic field. The beam is bent through a ninety degree angle and continues to the final set of electro-static focusing elements. These elements are, in principle, the same as the ones before the magnet and are used to refocus the beam which is tending to diverge as it leaves the magnet chamber. A schematic drawing of the apparatus is shown in Figure 1, while the exterior is shown in Plates I and II.

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Photograph of Apparatus, Rear View
FIG. 1 NEGATIVE ION APPARATUS
(Schematic)
The beam leaving these final collimating elements is well-defined, of constant charge-to-mass ratio, and approximately mono-energetic. It is allowed to enter a scattering region containing the scattering gas at some accurately measured low pressure and then passes into a Faraday cage, C in Figure 1, which collects the transmitted current. The scattered current is collected on the scattering elements, S and SL.

The scattering elements are a plate, SL, and a cylinder, S, both of which are concentric with the beam. The plate may be either at the same potential as the cylinder (and also the Faraday cage) or may have a small potential applied so as to either remove slow particles formed by inelastic collisions or to repel all negative particles.

The currents to the scattering cylinder, and collecting cage are determined by the amplifiers described by Searcy (17). The maximum full-scale sensitivity is $5 \times 10^{-14}$ ampere. These currents are related to the effective cross-sections through the familiar Beer-Lambert equation expressed in terms of cross-section, path length, and pressure (see Appendix I).

Several important modifications in the apparatus have been made. The filament is now of iridium cataphoretically coated with thorium (18). Each of three coatings was applied at 30 milliamperes for 15 seconds. Before coating, the ends of the filament were spot-welded to 5 mil nickel sheet for support in the filament clamps. The filament
emission to the anode is now regulated by a circuit adapted from the thyratron control portion of a standard ion gauge circuit (19). Finally, the repeller, $R_2$ in Figure 1, potential has been stabilized using two voltage regulator tubes (type OA-3) in series.

The thoriated filament was used in preference to the tungsten previously used in order to obtain a higher ion beam intensity. It has been found possible to obtain more than ten times the beam intensity from water vapor at 3 mm. backing pressure (at N in Figure 1) than from hydrogen gas at 6 mm. pressure. However, the life of the tungsten filament in water vapor was reduced to less than the time for an average run, whereas the thoriated iridium lasted about ten times this long.

The hydride ions produced from water vapor gave the same cross-sections as those obtained using hydrogen in the ion source.

The water vapor was in dynamic equilibrium with carefully degassed, distilled water maintained at approximately 0° C. by a Dewar flask containing an ice-water mixture. It was not necessary to maintain the temperature perfectly constant since small changes in the backing pressure affect the total current rather than the fractions scattered or transmitted.

One additional improvement was made. The oscilloscope used in preceding work was replaced with a General Radio type 1231-B null-detector, for locating the null point in the determination of the magnetic
field used to bend the hydride beam. The field is determined by balancing the potential developed by a constant-speed coil placed in the field against a reference voltage.

Figure 2 shows schematically the electrolytic cell, gas train, and leak system used for producing and introducing the oxygen into the scattering region. The electrolyte used in the cell was a 5% solution of barium hydroxide (Baker and Adamson reagent grade). This was chosen in preference to the potassium hydroxide used in previous work to prevent possible formation of carbon dioxide with the oxygen. Other possible impurities were presumed to be hydrogen, water, ozone, and hydrogen peroxide. To remove these from the oxygen, the gas was passed through a chain consisting of a platinum filament electrically heated to redness (to catalyze water formation between the oxygen and any hydrogen present), a silver-foil packed tube (to catalyze peroxide and ozone decomposition), and a phosphorous pentoxide tube (to remove water vapor present).

The oxygen was then passed into an intermediate pressure region constructed so that it could be pumped on through either or both of two capillaries of different lengths. These were connected to a mercury diffusion pump through a trap cooled by liquid air. From the intermediate pressure region, another capillary permitted the oxygen to enter the scattering region. It was possible with the arrangement used to
Fig. 2—Electrolysis Cell
obtain equilibrium pressures in the range $0.5 - 3.0 \times 10^{-3}$ mm. of mercury. This was adequate for the purpose.
CHAPTER IV

EXPERIMENTAL PROCEDURE

In order to remove residual traces of gas from the apparatus before scattering measurements were started, the entire apparatus was evacuated by four high speed mercury diffusion pumps as described by Muschlitz, Bailey and Simons (16). The pumping was continued until the pressure was of the order of 2 or $3 \times 10^{-5}$ mm. of mercury as measured by the ionization gauge before the measurements began. The coolant used on the pump traps was liquid air which expedited rapid removal of condensible gases from the apparatus and prevented mercury vapor from entering the system. When the pressure reached this value, the ion source chamber was opened to the water vapor, and the filament and anode voltages applied. The ion beam was focused to the Faraday cage by varying the magnetic field and adjusting the focusing elements for maximum ion intensity.

The method used in the past to determine ion velocity, i.e. a retarding potential on the final elements (20), was found impractical in the present apparatus. An energy correction, $\Delta V$, applied to the
potential difference between magnet chamber and cathode was determined in two ways. The first method utilized the mass spectrometer equation:

\[(4.1) \quad \frac{m}{e} = \frac{H^2 r^2}{2V} \quad \text{or, since } r \text{ is an apparatus constant, and } m/e \text{ is constant for } H^+,\]

\[(4.2) \quad V = kH^2. \text{ Since } V_M = V + \Delta V, \text{ it follows from (4.2) that} \]

\[(4.3) \quad V_M = kH^2 + \Delta V\]

Thus, plotting the square of the magnetic field needed to focus the hydride beam for maximum intensity against the potential of the magnet chamber, as measured in volts, gives a straight line with intercept equal to the velocity correction in volts. The magnetic field is expressed in arbitrary units in terms of the reading, \(D\), of a Helipot which is placed across a known reference potential, \(E_m\). \(D\) \(\hat{E}_m\) = \(E_m\) which is proportional to \(H\). Therefore, the actual plot was based on the relations

\[(4.4) \quad V_M = k'\hat{E}_m^2 + \Delta V = k'\hat{E}_m^2 D^2 + \Delta V\]

Equation (4.4) will give the same intercept as would equation (4.3). The different slope is immaterial to the determination of the
energy correction. Table I together with Figure 3, illustrate a plot of the data as used in this research.

The second method of determining the energy correction was to measure the total current at a number of voltages in the vicinity of zero ion energy and extrapolate these voltages to zero total current. Since the energy resolution at the magnet potential used was $\pm 3$ e.v., the extrapolated voltage was increased to 3 e.v. and this value was averaged with that obtained by the first method to give a value of $\Delta V$. This process was then repeated at the end of each run to account for any changes in conditions. The average of the two values obtained was taken to correct all points during the run. These values were self-consistent within 0.5 e.v. over a twenty hour run.

As a compromise between maximum beam intensity (with an energy resolution of $\pm 6$ e.v.) obtained with the magnet chamber maintained at 395 v. positive with respect to the cathode and smaller beam intensity (with better resolution), the magnet chamber was maintained at approximately 250 e.v. positive with respect to cathode during the scattering measurements. This gave the 3 e.v. resolution mentioned above.

Source conditions were maintained essentially constant during a given set of data in order to preserve the constancy of the ion energy in so far as possible.
### TABLE I

**FLUXMETER DATA**

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<tr>
<th>$V$ (e.v.)</th>
<th>$E$ (arbitrary units)</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>4.16</td>
</tr>
<tr>
<td>280</td>
<td>4.00</td>
</tr>
<tr>
<td>260</td>
<td>3.82</td>
</tr>
<tr>
<td>240</td>
<td>3.63</td>
</tr>
<tr>
<td>220</td>
<td>3.44</td>
</tr>
<tr>
<td>200</td>
<td>3.24</td>
</tr>
<tr>
<td>180</td>
<td>3.02</td>
</tr>
<tr>
<td>160</td>
<td>2.78</td>
</tr>
<tr>
<td>140</td>
<td>2.52</td>
</tr>
<tr>
<td>47.09</td>
<td>0.00*</td>
</tr>
</tbody>
</table>

* Method of least squares.
Fig. 3--Fluxmeter Graph
To investigate the possibility of multiple scattering in the pressure range covered, data for $R_S^0/R_S$ were plotted as a function of

$$\frac{\alpha_T^P}{F} = 10^{-1} = \frac{R_T^0}{R_T} - 1$$

This plot is given in Figure 4. The linearity of the plot shows $\alpha_S/\alpha_T$ to be pressure independent in the pressure range $0 - 3 \times 10^{-3}$ mm.

One important change in technique used in this experiment was the evaluation of the $R_T$ ratios at a negative lid potential. This potential was -4 v. for higher energies than 50 v. and -2 v. for lower energies. That this is justified may be seen by referring to Figure 5 in which $R_S^0/R_S$ is plotted as a function of the lid potential. Below -1 v., the ratio is seen to become essentially constant. Since the negative potential prevents slow negatively charged particles from reaching the lid, this ratio is very nearly equal to $R_T^0/R_T$. The total ratios taken in this fashion are probably more accurate than those obtained by the more labo-

rious method used in the past. This was to connect the lid, SL, to the scattering cylinder, and measure the current to the two while they were maintained at amplifier ground potential. Under these conditions it is possible that slow particles produced in the defining cylinder will be measured on SL. The present method enables the elastic cross-section to be obtained under the same experimental conditions, except for this
Fig. 4 -- Pressure Dependency Graph
Fig. 5—Lid Potential Graph
lid potential, as the total cross-section. Therefore, it offers large advantages over the prior method, as regards accuracy and convenience of measuring.

A first-order correction factor was applied to the $R_S^0/R_S$ data, in view of the constancy of the slope at high positive potentials in Figure 5. This was the extrapolation of the experimental ratios to zero lid potential to account for loss in the beam due to the defocusing action exerted by this potential on the elastically scattered ions. The action of this correction was to increase the value of the elastic cross-section by about 10 per cent. The extrapolation was carried out on the assumption that the slope of the linear portion of the curve was independent of the ion energy. This was found approximately true by experiment. The same behavior of $R_S^0/R_S$ has been observed for the previous work on the scattering of hydride ions in hydrogen (16). It is therefore reasonably certain that this is an apparatus effect rather than a physical phenomenon.

The method followed in taking the current ratios was to admit the oxygen to the scattering cylinder and to allow the pressure to equilibrate before slowly filling the McLeod gauge. The pressure measurements have been estimated to be accurate to $\pm 1.0\%$ in the range measured. After equilibrium was established, from three to eleven ratios were taken at each energy. The average value of these readings
was taken as the "R" value for that energy. The oxygen was then shut
off from the scattering region and, after establishing equilibrium,
readings were taken for the "empty tube" or "R^0" values at the lowest
apparatus pressure attainable.

The pressure measurements were obtained in a carefully
calibrated McLeod gauge of 500 ml. capacity in the following way:
the average capillary correction for the pressure range employed was
determined as an average of from three to twelve readings; this value
was then subtracted from the scattering pressure reading which was
obtained in the same fashion. The capillary correction was taken at
the same pressure as the "empty tube" ratios. The scattering pres-
sure measurement was made each time gas was admitted to the scat-
tering tube. All measurements of cross-sections were made in the
vicinity of 1.4 x 10^{-3} mm. of mercury. This pressure gave ratios
which were in the optimum range of 0.6 - 0.8, i.e. about 30 per cent
of the beam scattered. If more than 60 per cent of the beam is scat-
tered multiple collisions will seriously affect the results.

When shutting down, the system was pumped to a pressure of
the order of 5 x 10^{-6} mm. of mercury by the diffusion pumps. The
pumps were then shut down and the system slowly filled with nitrogen
to one atmosphere pressure.
CHAPTER V

TREATMENT OF DATA

The results listed in Table 2 for the scattering investigated in this research show the interaction cross-section of the hydride ion and oxygen gas for three types of scattering. The data contained in this table are plotted in Figure 6 over the energy region investigated. The top curve shows the variation of the total cross-section with energy; the center one, that of the elastic cross-section; and the lowest one, the difference which is equated to the inelastic cross-section as discussed in Appendix I.

Analysis of Data for Elastic Scattering

This analysis is based on the four classical assumptions mentioned in Chapter II. The first of these, that interaction is attributable to a central force field, is expressed as an attractive inverse n'th power law of the particle distance.

\[ V = \frac{-K}{r^n} \]
<table>
<thead>
<tr>
<th>$V$ (e.v.)</th>
<th>$\Delta V$ (e.v.)</th>
<th>$R_S^0$</th>
<th>$R_S$</th>
<th>$R_T^0$</th>
<th>$R_T$</th>
<th>$T$ (°C)</th>
<th>$V_{SL}$ (e.v.)</th>
<th>$P_c \times 10^3$ (mm. Hg)</th>
<th>$a_T$ (cm$^2$/cm$^3$)</th>
<th>$a_S$ (cm$^2$/cm$^3$)</th>
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<td>0.736</td>
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<td>0.623</td>
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<td>0.660</td>
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<td>Rₜ</td>
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<td>qₜ (cm²/cm³)</td>
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Fig. 6—Cross-sections as Functions of Ion Energies
The second assumption is that the oxygen molecule is initially at rest with respect to the hydride ion. Since one has thermal energy and the other has energy of at least several volts, this is certainly valid. The third assumption is that the system is conservative. This assumption is probably true at low energies, but becomes less safe at higher energies. As previously stated, the simplifying assumption is made that the scattering angle is small. This assumption is certainly not true for those ions which were scattered as they were about to leave the scattering cylinder; however, most of the scattering occurs in the upper half of the scattering cylinder since the beam intensity drops in an exponential fashion. It has been shown by Kells (7) that a treatment of scattering data based on the assumption that the cosecant of the relative scattering angle equals the cotangent of that angle gives results which agree within one per cent of an exact treatment described by Simons, Muschlitz, and Unger (8).

For the system hydride ion - oxygen molecule, the hydride ion may be considered as having an initial velocity $v_0$ and mass $m_1$; while the oxygen molecule will be treated as a single particle of mass $m_2$, initially at rest.

The distance between the particles is defined as $r$, with the distance of closest approach defined as $r_0$. The relative scattering angle referred to the molecule is taken as $\theta$. 
Since the system is a conservative one, defining $\beta$ as the relative radial angle,

\begin{equation}
(5.2) \quad \mu \frac{x^2}{\beta} = \mu v_0 b = \text{a constant, where } \mu \text{ is the reduced mass and } b \text{ is the impact parameter. The relative total energy of the system is}
\end{equation}

\begin{equation}
(5.3) \quad E = \frac{\mu}{2} (\dot{x}^2 + \frac{r^2}{\beta^2}) + V = \frac{1}{2} \mu v^2.
\end{equation}

Substitution of (5.1) gives

\begin{equation}
(5.4) \quad E = \frac{\mu}{2} (\dot{x}^2 + \frac{r^2}{\beta^2}) - \frac{K}{r_0} = \frac{1}{2} \mu v^2.
\end{equation}

Since $\dot{r} = 0$ when $r = r_0$, equation (5.4) may be solved for the impact parameter, $b$,

\begin{equation}
(5.5) \quad b^2 = r_0^2 + \frac{K}{E} r_0^{2-n} \quad \text{and, averaging over the scattering length, "1",}
\end{equation}

\begin{equation}
(5.6) \quad b_a = \frac{\int_0^\infty \frac{1}{r_0^2} \frac{dv}{dx} \frac{K}{E} \int_0^\infty \frac{1}{r_0^{2-n}} \frac{dx}{dx}}{\int_0^\infty \frac{1}{r_0^n} \frac{dx}{dx}}
\end{equation}
\[ a_S = \frac{N \pi b_a^2}{n} \left( \frac{1}{n+2} \right) \left( \frac{E(b)}{E} \right)^{2/n} \]

Relating the minimum absolute scattering angle,

\[ \phi = \tan^{-1} \left( \frac{a}{1^1} - x \right) \], where \( a \) is the radius of the scattering cylinder

hole, to the relative energy, \( E \),

\[ \tan \theta = \frac{K \pi^2 \Gamma (n/2 + 1/2)}{E \Gamma(n/2)} = \frac{K^2 \pi^2}{E \Gamma(n/2)} \]

applying the assumption of small angle scattering to the equation

relating the relative and absolute scattering angles

\[ \cot \phi = \cot \theta + \frac{m_1}{m_2} \csc \theta \cdot \frac{m_1}{\mu} \cot \theta \]

The measured ion energy is \( W = 1/2 m_1 v_0^2 \).

Equation (5.7) now becomes

\[ a_S = N \pi b_a^2 \left( \frac{1}{n} \right) \left( \frac{E(b)}{E} \right)^{2/n} \]

\[ + N \pi a n m_1 \left( \frac{E(b)}{E} \right)^{2/n} \left( \frac{K}{W a} \right)^{2/n} \]
from which

\[(5.11) \quad \frac{\alpha}{S} \frac{W^{2/n}}{n} = Q = N \pi n \left( \frac{KC''1}{a} \right)^{2/n} \left( \frac{1}{n+2} + \frac{m_1}{2\mu C''1} \right). \]

Upon taking logarithms of the first equation (5.11),

\[(5.12) \quad \log \frac{\alpha}{S} + \frac{2/n \log W}{n} = \log Q \text{ follows.} \]

This last equation shows that a plot of the logarithm of \( \alpha_S \) against the logarithm of the ion velocity should be a straight line with slope of \(-2/n\) and intercept of the logarithm of \(Q\). The intercept, \(\log Q\), is used in evaluating the constant of the potential law from equation (5.11). It should be stressed that this law will hold only for the region where all assumptions are valid. A plot of (5.12) for hydride ions in oxygen from 3-20 volts is given in Figure 7. From this plot, the slope was found to be \(-0.072\) and the intercept, 1.79. By utilizing the preceding equations, the potential function for this range \((b_a = 2.0 - 2.3 \, \text{A})\) has been evaluated as

\[(5.13) \quad V = - \frac{10 + 220}{r^{28}} \quad \text{with} \, r \, \text{expressed in centimeters, and} \, V \text{ in electron volts.} \]

The previous work on the scattering of low velocity hydride ions was in hydrogen; in which, there is no tendency for compound formation. The \(H^- - H_2\) interaction appeared to follow an ion-dipole
Fig. 7--Potential Law Graph at Low Energies
(n = 4) type of attraction at low energies. The high value of the exponent in the potential law observed for oxygen at these low energies is attributed to a short range attractive force arising from a valence (or exchange) interaction between H\(^+\) and O\(_2\). It would seem that the data indicate H\(_2\)O\(^-\) to be a stable structure. This ion has been known to exist in solution for some years as the anion of hydrogen peroxide (20).

The minimum in the elastic curve may be a typical property of negative ion scattering since it has now appeared in both cases investigated. For the hydride-hydrogen case, the minimum appeared at about 55 volts and showed a gradual rise thereafter. In the present case, as is shown in Figure 6, the minimum occurred at about 20 volts ion-energy and the cross-section then showed a gradual rise to about 100 volts. Since this minimum was found at an ion energy of twenty volts, it is quite possible that excitation of the oxygen molecule takes place at higher energies. An excited electronic state, \(^1\Delta_g\), having an energy of about 1 e.v. above the ground state is known for oxygen (21). It would appear that this is a probable explanation of the rise in the cross-section at higher energies. Such an excitation would appear in the elastic measurement since the inelastically scattered ion will still retain considerable kinetic energy.

The excitation postulated in the case of the hydride ion - hydrogen molecule scattering (16) involves the excitation of the molecule to
the $^1 \Sigma_u$ state. As this lies about 11 e.v. above the ground state of hydrogen, the maximum probability for this excitation should occur at a higher ion energy than should the excitation of oxygen postulated in the present research. Comparison of the present data with those obtained in the scattering in hydrogen bears out this theory. The elastic cross-section for the hydride - hydrogen system is still increasing at 400 e.v. ion energy.

A search for positive ion formation was made at 400 e.v. ion energy by measuring the current to the scattering lid when various negative potentials were applied to the lid. Since the ionization potential of oxygen is 12.5 e.v., no detectable ionization was anticipated at this energy and no current was measured to the lid.

The inelastic cross-section curve qualitatively resembles that obtained in the hydrogen scattering data above twenty volts. In the light of the conclusions reached in that experiment, and also those obtained by Hasted (11), it seems reasonable to conclude that the process taking place above twenty volts is principally "ionization" of the hydride ion according to the general type of equation (1.10).

The inelastic cross-section for the system $\text{H}^- - \text{H}_2$ tended to approach zero at lower energies. A similar behavior was noted by Hasted (11) for the inelastic scattering of $\text{H}^-$ in the rare gases. In the present research, the inelastic cross-section appears to rise below
twenty volts ion energy. Because of the rise in cross-section at lower energies and because of the low absolute value of $\Delta E$ for the exchange process, it seems reasonable to assume that the primary process which is taking place in this neighborhood is the charge exchange phenomenon,

$$(6.1) \quad H^- + O_2 = H + O_2^- + \Delta E.$$  

$\Delta E$ is the energy difference between the electron-affinity of atomic hydrogen and that of molecular oxygen. The probability of such a process increases with a decrease in the absolute value of $\Delta E$. Values for the electron affinity of molecular oxygen vary, but, assuming an approximate value of 0.9 e.v. and using 0.75 e.v. for the electron affinity of the hydrogen atom there is obtained an absolute value of 0.15 e.v. for the energy difference.

An estimate of the probable error in the determination of the potential law, equation (5.13), may be made assuming 0.5% error in $\mathcal{R}_T/\mathcal{R}_T^0$ and $\mathcal{R}_S/\mathcal{R}_S^0$, 1% error in the pressure measurements, and $\pm 1$ e.v. uncertainty in the ion energy. The probable errors in $\alpha_T$, $\alpha_S$, and $\alpha_I$ are 1.5%, 4%, and 8% respectively. The resulting probable error in the exponent, $n$, is $\pm 7$. It is difficult to make an estimate of the error due to the influence of inelastic scattering on the elastic cross-section. This will be appreciable at ion energies above 20 e.v. At very low ion energies the assumption that the
initial momentum of the oxygen molecule is negligible is questionable. It is felt, however, that the overall uncertainty in the exponent is not much more than ±10.
CHAPTER VII

CONCLUSIONS

Investigations have been made of the scattering cross-sections of hydride ions in gaseous molecular oxygen in the energy range of three volts to one-hundred-and-sixty volts incident ion energy. The cross-sections for both the elastic and inelastic types of collision were investigated and the results point to the following conclusions.

In light of the elastic scattering results, it seems quite reasonable to assume that in the low energy region there is a tendency for formation of the $O_2^-$ ion. The potential expression which best fits the data is

$$V = -\frac{10^{-220}}{r^{28}}$$

over the range of interaction 2.0 - 2.3 A. It is possible that this type of behavior is a general one for negative ion collisions in which valence or exchange forces are involved. Above twenty volts, the interpretation is complicated due to a rise in cross-section which is attributed to excitation of the molecular oxygen at the expense of kinetic energy from the ionic beam.
The inelastic cross-section goes through a much sharper minimum in the same region as the elastic scattering minimum. The lower energy cross-sections are attributed to charge exchange between the ion and the molecule while the higher energy cross-sections are primarily the result of simple detachment of the electron from the ion to form a hydrogen atom.
APPENDIX I

(1) \( I_x = I_0 \exp \left( -\alpha_T x p \right) \) where \( I_x \) is the current at distance \( x \) along the scattering path compared to \( I_0 \), the current at the start of the scattering path; \( \alpha_T \) is the total cross-section for the interaction (which may be attractive or repulsive); and \( p \) is the pressure of scattering gas. Since all collisions are either elastic or inelastic the total cross-section may be equated to the sum of the elastic and inelastic cross-sections. Differentiation of (1) gives

(2) \(-dI_x = dI_T = I_x \alpha_T p dx \) which, together with additivity of the cross-sections, gives rise to

(3) \(-dI_x (\alpha_s) = I_x \alpha_s p dx \) and

(4) \(-dI_x (\alpha_I) = I_x \alpha_I p dx \).

Division of (3) by (2) results in

(5) \( \frac{d}{d} \frac{I_x (\alpha_s)}{I_x (\alpha_T)} = \frac{\alpha_s}{\alpha_T} \).

Integrating over the scattering length and indicating the total scattered current by \( I_T \) and the elastically scattered current by \( I_E \), gives
\[ (6) \quad \frac{I_E}{I_T} = \frac{a_s}{a_T} \]. Similarly, \[ \frac{I_I}{I_T} = \frac{a_I}{a_T} \] where \( I_I \) is the inelastically scattered current.

Due to the design of the scattering region, all particles which are not sufficiently deflected from the beam path will go to the Faraday collecting cage and be counted as transmitted current. Essentially all other ions will be collected on either the scattering cylinder or the lid of the cylinder. The currents to the collecting cage, the scattering cylinder and the lid of the scattering cylinder may be represented by \( I_C, I_S, I_{SL} \), respectively when the total ratios are being taken. When the retarding potential is applied to the lid, \( I_S \) and \( I_{SL} \) become \( I_S' \) and \( I_{SL}' \).

Since it is far simpler to work with fractions of the total current than it is to calculate absolute currents as indicated by a potential drop across a high resistance, it is found convenient to define the following fractions:

\[ (7) \ a) \quad R_T = \frac{I_C}{I_S + I_C + I_{SL}} = \frac{I_C}{I_C + I_T} \]

\[ b) \quad R_S = \frac{I_C}{I_S' + I_C} = \frac{I_C}{I_C + I_E} \]

\[ c) \quad R_I = \frac{I_C}{I_{SL}' + I_C} = \frac{I_C}{I_C + I_I} \]
Equations (7) may be rearranged to give

\[(8) \quad a) \quad \frac{1}{R_T} - 1 = \frac{I_S + I_{SL}}{I_C} = \frac{I_T}{I_C} \]

\[b) \quad \frac{1}{R_S} - 1 = \frac{I_S}{I_C} = \frac{I_E}{I_C} \]

\[c) \quad \frac{1}{R_I} - 1 = \frac{I_{SL}}{I_C} = \frac{I_I}{I_C} \]

In light of equations (6),

\[(9) \quad a_S = \frac{1}{R_S} - 1 \quad a_T \quad \text{and} \quad a_I = \frac{1}{R_I} - 1 \quad a_T \]

Rearrangement of (1) gives, with the length "l",

\[\ln \frac{I_0}{I_C} = p \alpha "l" \quad \text{therefore} \]

\[(10) \quad a_T = \frac{1}{P"l"} \ln \frac{I_0}{I_C} = \frac{1}{P"l"} \ln \frac{1}{R_T} \]

The actual equation used, however, was one based on scattering at two different pressures; to account for small errors in alignment, beam spread due to space charge effects. One of these pressures was the lowest vacuum pressure obtainable and gave a scattering ratio, $R_T^0$, very close to one. The corrected equation became:
(11) \[ \alpha_T = \frac{T}{(273.2^\circ K) "1" (P - P_0)} \ln \frac{R_T^0}{R_T} \]

\[ = \frac{F}{P - P_0} \log \frac{R_T^0}{R_T} ; \text{where} \]

\[ F = \frac{T(2.303)}{273.2^\circ K "1"} \]

This same correction is applied to the \( R_S \) values; i.e., \( R_S^0 \) ratios which were close to unity were used to obtain \( \alpha_S \). Since \( \alpha_I = \alpha_T - \alpha_S \), it is not essential to measure \( I_{SL}^I \) separately in order to evaluate \( \alpha_I \).
## APPENDIX II

**Definition of Symbols**

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<td>C (Ion Source)</td>
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<td>Nozzle</td>
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<td>R₁, R₂</td>
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<td>SL</td>
<td>Scattering Cylinder Lid or Plate</td>
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<td>Scattering Pressure in mm of Hg</td>
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<tr>
<td>$W$</td>
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BIBLIOGRAPHY

1. Tüxen, Z. Phys. 103, 463, (1936)
10. Amdur and Pearlman, J. Chem. Phys. 8, 7, (1940)


25. Massey, op. cit., p. 28
VITA

John Murray McGuire was born in New Bedford, Massachusetts, on 15 May, 1929. He is the son of Mary Murray McGuire and the late Thomas Christopher McGuire, Jr. He graduated from Belmont Abbey Preparatory, Belmont, North Carolina, as Valedictorian in 1945. He then entered the University of Miami, Coral Gables, Florida, from which he received the Bachelor of Science degree cum laude in 1948 and the Master of Science in 1951. He then entered the Graduate School of the University of Florida, Gainesville, Florida.
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

January 29, 1955

[Signature]
Dean, College of Arts and Sciences

[Signature]
Dean, Graduate School

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