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SCATTERING OF POSITIVE LITHIUM IONS IN MERCURY VAPOR

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Abstract

The number of positive lithium ions passing through a fixed distance was observed with different pressures of mercury vapor. The rate of absorption deduced was found to depend on the aperture of the apparatus. This indicates that the absorption is due largely to small angle scattering of the ion at a collision with a mercury atom. This scattering is incompatible with that due to elastic collisions. A computation with a law of electrostatic repulsion gives a dependence of absorption on aperture in qualitative agreement with the observations.

IN THE usual experimental arrangements the absorption of positive ions in gases may be due to change in velocity, either in direction or in magnitude; or to neutralization, either from collision with gas molecules or by picking up free electrons. Durbin,[1] Ramsauer,[2] Kennard[3] and others have studied slow speed positive ions in hydrogen, helium, neon, nitrogen, air, oxygen and argon. The methods actually used by Durbin and Ramsauer measured those ions which had not been removed by any of the effects mentioned above. Kennard's modification of Durbin's method makes possible the detection of change in speed. For instance, he found for 90 volt caesium ions in hydrogen a decrease in speed equivalent to 1.3 volts per collision. In this one case the area under the curves was constant for the pressure range 0.2×10^{-4} to 80×10^{-4} mm Hg, indicating the complete absence of neutralization and scattering.

Slowing up accompanied by a tendency toward equality in areas was observed for 35 and 90 volt caesium ions in both hydrogen and helium and also for rubidium ions in hydrogen. This indicates that slowing up is to be expected in the case of heavy ions in light gases. For caesium in argon, however, symmetrical curves having approximately the same base-line were observed. Kennard interpreted these curves as showing that the main phenomenon was neutralization of the ions, since if scattering were the cause of absorption one would expect deviations both to larger and smaller radii of curvature, with the result that curves taken at higher pressure would have longer base-lines. When the dimensions of the absorbing chamber are considered ($20\times128\times3$ mm^3) one sees that scattering is not ruled out on this ground because the number of ions scattered along the armature slot may be negligible compared with the number scattered into the pole piece which

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[1] Durbin, Phys. Rev. **30**, 844 (1927).

[2] Ramsauer, Phys. Zeits. **28**, 858 (1927).

[3] Kennard, Phys. Rev. **31**, 423 (1928).

form its walls, so that the electrometer current may decrease so sharply on either side of the peak as to make the curves seem to have the same baselines as in Fig. 3 below. For these cases in which Kennard concluded that the absorption was due to neutralization with no loss of speed, there was therefore no conclusive evidence to differentiate between scattering and neutralization.

In the present experiments lithium ions were passed through mercury vapor in order to study the case of a light ion in a heavy gas. The absorption was observed by two distinct methods which, taken together, permit of a conclusion as to the cause of absorption. For those cases which show no definite speed change it is possible to determine whether scattering is playing an important role in the absorption. It was found in these experiments that the behavior of positive ions is not the same as that of electrons in absorption experiments. The indentity of "Absorbierender Querschnitt" and "Wirkungsquerschnitt" as found by Ramsauer[4] for electrons does not hold for positive ions. That is, the "opposing cross section" when measured by an apparatus of the Mayer[5] type is less than when measured by one of the Ramsauer type. This fact prevents any definite meaning being given to the radius of ions or molecules as determined in this way.

APPARATUS

The usual method of using mercury vapor at low pressure is to put the trap of the diffusion pump into a thermostat and assume that the mercury vapor diffuses back into the apparatus at a pressure corresponding to the temperature of the trap, while air, water vapor and gases from metal parts diffuse the other way and are removed. While this would possibly be the equilibrium condition, it would be only slowly realized in a perfect apparatus and perhaps not at all in cases where the ion source gives out considerable gaseous material as it emits. A continuous flow method involving a small mercury well, a hot wire gauge, and magnetically operated throttle valve which controlled the rate of pumping was first tried. It was abandoned because the gauge would not stay in calibration long enough to take data for a complete set of curves.

At Professor Dempster's suggestion the method shown in Fig. 1 was adopted. The mercury well Hg is 5.5 cm in diameter and the glass tubing of the vacuum line 1.2 cm in diameter with an effective length from well to liquid air trap T'' of about 200 cm. A careful attempt was made to place the analyzing chamber A at exactly the mid-point of this glass line resistance so that the pressure in this chamber is just half of that in the well, when the trap is in liquid air. This gives a high speed vacuum system which is constantly flushed with mercury vapor. When a high vacuum is required liquid air is placed also on trap T.

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[4] Ramsauer, Ann. d. Physik **64,** 513 (1921).

[5] Mayer, Ann. d. Physik **64,** 451 (1921); Also P. Lenard; Wien's "Handbuch der Experimentalphysik" XIV, 170 (1927).

The temperature regulator was an ether vapor thermometer (using a mercury column in vacuo to balance the ether vapor pressure) with 7 electrodes sealed in a long capillary as at *F* in Fig. 1. These were connected through an 8 point switch and sensitive relay to the heater circuit. Each position of the switch gave a constant temperature. The range was from −30°C to 46°C. This regulator was placed beside the mercury well Hg in a thin copper cylinder, *R*, which acted as a baffle. Twelve wood splints, *I*, resting on the bottom of tall glass beaker, *J*, served to support the baffle and to hold the heater wire, *W*, in the convection stream. The glass beaker was supported by its flange in a second cylinder, *L*, which acted as a baffle for convection currents in the cooling bath, *N*. Kerosene was used in the beaker. Dried air from copper tubes, *Q*, provided convection currents in both beaker and pail. The heavy arrows indicate the directions of these currents. By keeping the cooling liquid in the refrigerating pail to within 5° of the desired temperature on the low side, and by using a large surface of heater wire whose temperature while carrying current is regulated (by a potentiometer hook-up) to a few degrees above the desired temperature, the regulation can be made to 0.1° with certainty and probably much better. The temperature of the room was kept several degrees higher than the highest temperature in the thermostat to avoid condensation of mercury on the walls —generally at 52°C. Knudsen's[6] values for the vapor pressure of mercury were used.

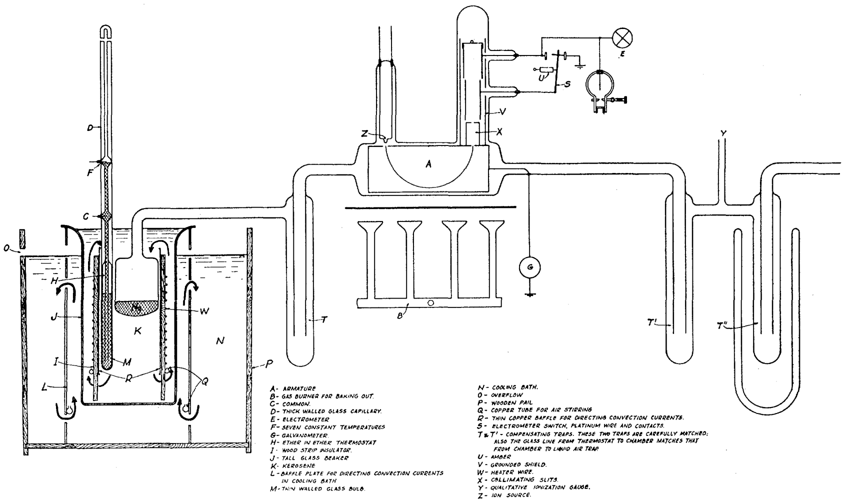

Fig. 1.

The lithium ion source was that used by Hundley[7] and Thompson: A small crystal of spodumene fused on to a platinum strip heater.

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[6] Knudsen, Ann. d. Physik **29,** 184 (1909).

[7] Hundley, Phys. Rev. **30,** 864 (1927).

This source is remarkably constant in emission for long periods. This is evident in the fact that the experimental points for the electrometer current with different currents through the magnet, lie on a smooth curve and that these curves were reproducible from day to day as shown for example in the data for lithium at 25 volts. The source seems to be much steadier than the lithium amalgam source used by Ramsauer as shown by the wide distribution of experimental points in his curves[2] and the necessity for rapid observations mentioned in his papers. The galvanometer used to measure the initial ion current had a current sensitivity of the order of 10^{-10} amps. per mm when critically damped. The usual deflection was 100 mm so that initial ion current could be maintained easily to 1 percent. The Faraday-cylinder ion-currents were measured using Dempster's[8] balance method, with a quadrant electrometer of 1100 divisions per volt sensitivity as a null indicator. The leads to this were short and carefully shielded—the only insulation being the glass of the line, the amber of the electrometer and a single sulphur plug at the ionization chamber. The apparatus was enclosed entirely in glass—the high temperature of the room and the necessity for frequent baking out prohibiting the use of waxed joints. A three stage mercury pump was operated continuously, and data were taken after the apparatus had been pumped for several days.

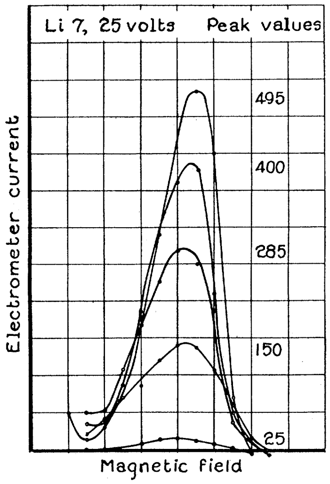

Fig. 2.

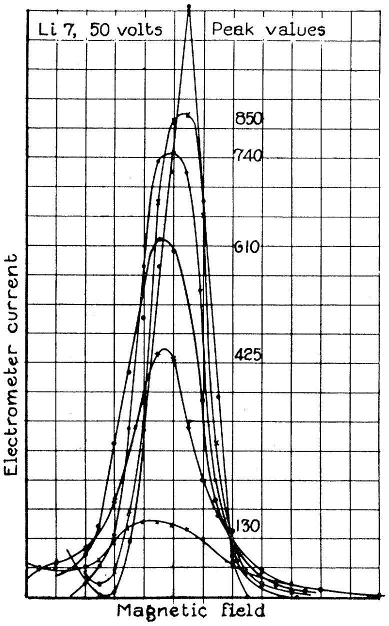

Fig. 3.

Two methods of procedure were followed designated as the first and second methods.

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[8] Dempster, Phys. Rev. **18**, 417 (1921).

First Method

The procedure for the first method was that described in detail by Kennard.[3] The total ion current, as indicated by the galvanometer, was kept constant while data were taken for a set of 5 curves at a single accelerating potential. Each curve of the set shows the variation of electrometer current with magnetic field current for a particular pressure. Examples of the curves so obtained with lithium ions in mercury vapor are shown in Figs. 2 and 3. They are in most cases symmetrical about the same value of magnetic field current—indicating that the ions do not lose speed in these cases.

Peak values were used in computation, although the whole curve was always taken to make sure that unnoticed changes in magnetic field or accelerating potential had not influenced the peak values. Several sets of curves for different pressures were taken for each accelerating potential. Each set contained 5 curves and gave 10 combinations of two pressures each, from which independent determinations of the absorption coefficient were made. A short derivation of the absorption equation follows:

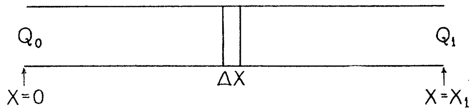

Fig. 4.

Consider a column of gas 1 cm^2 in cross section and X cm long, with $P_1N/760$ molecules per cc. Let its X dimension be along the x-axis and let it be traversed in the x-direction by Q positive ions. $-\Delta Q$ is the number of ions removed in distance ΔX. (R_1+R_2) is the greatest distance between ion-center and molecule-center which will cause absorption as the ion passes the molecule. In distance ΔX the fraction of unit area which will cause removal of an ion is $P_1N\pi(R_1+R_2)^2\Delta X/760$. This is the probability that an ion will be "absorbed." For Q ions, an integration gives:

$$Q_1=Q_0e^{-P_1X_1[\pi N(R_1+R_2)]/760}.$$

The absorption coefficient is here called λ^+ and is:

$$\lambda^+=[N\pi(R_1+R_2)^2]^{-1}.$$

It corresponds to the mean free path of the kinetic theory and here means that an ion would probably travel a distance λ^+ cm in the gas at atmospheric pressure without coming within (R_1+R_2) cm of a gas molecule—center to center.

According to this absorption equation for a curve at pressure P_1:

$$Q_1=Q_0e^{-P_1X_1/760\lambda^+} \tag{1}$$

in which Q_0 is the total ion current as read by the galvanometer in series with the accelerating potential. This is maintained constant for the whole set at a particular voltage. Q_1 is the peak value of the electrometer current and X_1 is the length of the absorbing path. For a second curve at higher pressure:

$$Q_2 = Q_0 e^{-P_2 X_1 / 760\lambda^+}. \tag{2}$$

Hence

$$Q_2/Q_1 = e^{-X_1(P_1-P_2)/760\lambda^+}$$

$$\lambda^+ = \frac{x_1(P_2-P_1)}{760 \times 2.3026 \log_{10} Q_1/Q_2}\,. \tag{3}$$

Equation (3) refers to absorption in which an ion is removed completely from the bundle when its center comes within the distance (R_1+R_2) cm of the center of a gas molecule.*

Ten values of λ^+ were calculated for each set of 5 curves taken in this way and the average taken as one determination of mean free path. Curve Fig. 5 shows how the observed values from Fig. 2 agree with the true exponential calculated from the average λ^+ deduced as explained above.

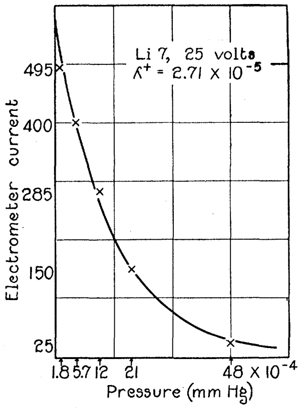

Fig. 5.

Five sets at a velocity of 25 volts gave for $\lambda^+ \times 10^5$ the values: 2.56, 2.64; 2.92, 2.81 and 2.71; with an average of 2.74. These observations were with a single source. Similar observations at 50 volts with two separate ion sources gave for $\lambda^+ \times 10^5$: 3.54, 3.32, 3.86, 4.39, 4.32, 4.49; with an average of 3.98. At 100 volts two series of curves gave $\lambda^+ \times 10^5 = 4.40$ and 4.17 with an average of 4.29; at 200 volts one series gave $\lambda^+ \times 10^5 = 5.4$.

The values of $\pi(R_1+R_2)^2$ which may be called the effective cross-section are plotted in Fig. 6, marked I, for various voltages. If the lithium ion radius is taken as that of the helium atom and one uses the values from viscosity measurements, $R_{\mathrm{He}} = 1.09\mathrm{A}$, $R_{\mathrm{Hg}} = 1.82\mathrm{A}$; $\pi(R_1+R_2)^2 = 26.6 \times 10^{-16}$. If the radius of the Li^+ is taken as Ramsauer takes it from crystal lattice values $R_{\mathrm{Li}^+} = 0.41\mathrm{A}$; $\pi(R_1+R_2)^2 = 15.6 \times 10^{-16}$. These values are shown by the horizontal broken lines of Fig. 6.

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* Note appended.

This curve seems to indicate that the ionic radius approaches the kinetic theory value (viscosity) at low voltage, as do the data of Durbin,[9] Thompson, and Kennard who worked with almost indentical apparatus in this laboratory. Ramsauer's interpretation of his experiments,[2] on the contrary, indicates that the radius sum approaches the crystal-lattice-value for the radius of the alkali ion at high voltage and increases as the speed is reduced. A modification of the experiment so far described gives experimental evidence tending to show that this discrepancy is due to the fact that these experiments are in general dependent on the dimensions of the apparatus; so that no absolute theoretical significance may be ascribed to the R_1 and R_2 deduced. The "opposing cross-section" deduced from this type of observation depends not only on the gas, the ion used and its velocity, but also on the dimensions of the apparatus used in making the observations.

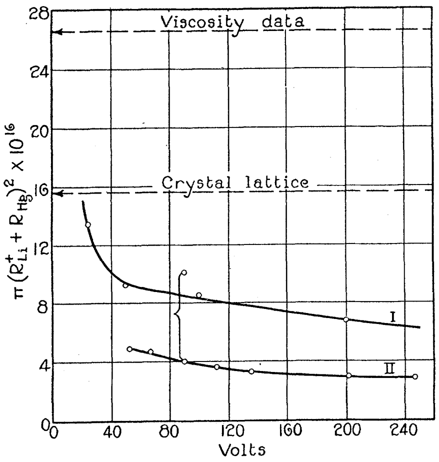

Fig. 6.

Second Method

In a second set of experiments two coaxial Faraday cylinders F_1, F_2, were used as shown in Fig. 1. These were connected so that the whole of the positive ion stream Q_0 entering from the analyzing chamber could be measured. The lower one was then earthed and only a few seconds later the part escaping absorption through a distance equal to the length of the lower cylinder (10 cm) was measured by the same electrometer. The apparatus gave zero absorption at "zero" pressure, that is, with liquid air on trap T as well as on T'', $Q_1 = Q_0$ or the electrometer current to the top cylinder alone is as large as it is when both are connected together and to the electrometer.

The experimental arrangement was originally devised to give a pure source of lithium ions. With this apparatus it was not necessary to alter the pressure and the apparatus was in equilibrium for days before readings

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[9] Curves in Fig. 8.

were taken. The absorption coefficient was obtained from the following equation.

$$Q_1 = Q_0 e^{-PX/760\lambda^+}.$$

Where both Q_1 and Q_0 are direct electrometer measurements. Values of $\pi(R_1+R_2)^2$ taken from these data are plotted on the curve in Fig. 6, marked II. It is seen that this value is much smaller than that obtained by the previous method, and in order to make sure that this difference was not due to low pressure in the apparatus, data were taken first by the second method and then by the first, raising the pressure and using the two Faraday cylinders coupled together as the collecting electrode. In this way it was possible to check from one curve to the other as shown by the bracketed points in Fig. 2. Repeated checks, between which the apparatus was baked to restore it to the lower pressure and left for more than 24 hours in order to come to equilibrium at the low pressure, showed that the apparatus still behaved normally with the first method. These checks always gave even larger values of $\pi(R_1+R_2)^2$ by the first method than previously obtained. As will be explained below this may be attributed to the added collimating slits in front of the second absorption chamber, for although X is corrected for the *distance* between these it cannot be corrected for the fact that they are of smaller cross-section. Their effect is to decrease the angular aperture of the apparatus and to increase the observed $\pi(R_1+R_2)^2$.

The difference in the two series of observations indicates that the absorption is largely a small-angle scattering phenomenon rather than one of neutralization or scattering in which an ion when deflected is thrown completely out of the bundle. The dimensions of the absorbing Faraday cylinder (3 cm diameter) in Method II are much greater than those of the armature slot (0.3×2) in which the absorption occurred in the first method. One would expect a smaller $\pi(R_1+R_2)^2$ with the larger absorbing chamber because a smaller part of the scattered cone of rays is intercepted. Values of $\pi(R_1+R_2)^2$ taken with Method II, using an absorbing Faraday cylinder of smaller diameter were intermediate between those shown in Fig. 6 for the first and second methods.

A further evidence of scattering is found in the fact that for any pressure there is a voltage below which the peak electrometer-current drops to almost zero no matter what the intensity of the ion current. The curve in Fig. 7 shows for a pressure 9×10^{-5} mm Hg the variation of peak electrometer-current with accelerating potential—the total to the first slit being left constant. There is a sudden change in the curve at 18.6 volts, the number of ions reaching the second slit at 17.2 volts being less than half that at 18.6. This suggests that there is a rapid variation in the small-angle scattering with the velocity of the ion at these low velocities. For higher pressures the velocity of the ions at which the rapid increase in scattering occurred was higher; and for lower pressure, lower. This means that as the pressure is increased a point is reached where practically none of the slow ions can make their way through the distance to the second slit without suffering a deflection greater than the small amount required to throw them to one side of the opening of the second slit.

In Ramsauer's experiments[2] the absorption takes place *at the slits* whereas, in these it occurs largely at the walls of the long narrow armature slot. This and the smallness of his apparatus show why he was able to work at lower accelerating potentials than is possible with this apparatus with light ions. If the force producing scattering is electrostatic it follows that the slower the ions the longer the time during which this force is operative and the greater the distance between electric centers for an angular deflection great enough to throw the ion out of the next aperture. Also the smaller the next aperture the greater the distance between electric centers at which an ion will be deflected just enough to be caught on the edge of the slit. It seems therefore, that the observed "effective cross-section of an ion" depends both on its velocity and the dimensions of the absorbing apparatus. Ramsauer,[10] Durbin, Kennard, Thompson and the author have observed this dependence on velocity. This experiment gives definite proof of the dependence of the effective cross-section on the dimensions of the absorbing apparatus for Li ions in Hg vapor. It seems therefore that absorption is, in this case largely due to scattering.

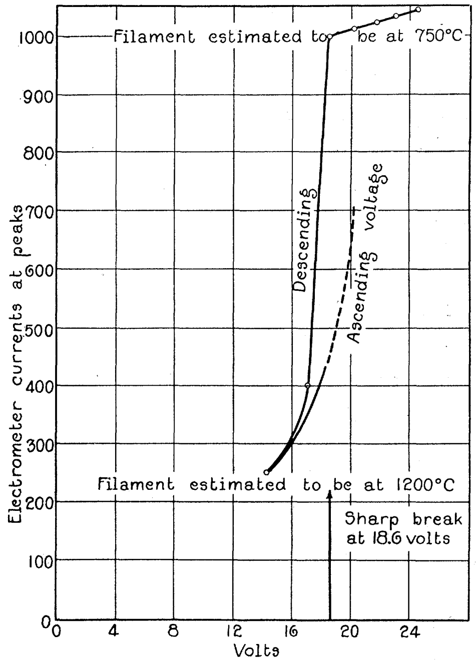

Fig. 7.

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[10] Ramsauer, however indicates that the "effective cross-section" approaches a constant value at about 16 volts. Durbin's data (reference 1) show that this is not the case. As Durbin's curves were taken with a larger apparatus than Ramsauer's, the numerical values would not be expected to check, although the general form of the curve would be independent of the apparatus.

In the case of analogous experiments on electrons, the agreement of Mayer's[5] and Ramsauer's[4] values for the absorbing cross-section showed that when an electron was deviated at all it was thrown completely out of the bundle. This conclusion was necessary because the angular aperture of the collecting chamber was much greater in Mayer's experiment than in Ramsauer's and small deviations if they had been present would not have decreased the intensity with Mayer's apparatus, while they would have thrown the electron out of the beam in Ramsauer's. The present experiments show that small-angle scattering does occur in the case of light relatively slow positive ions.

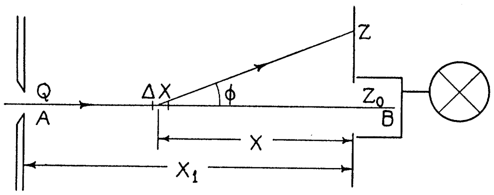

Fig. 8.

The author is indebted to Professor Dempster for the following analysis of the scattering to be expected with two different laws of force at collisions, showing the relative importance of small-angle scattering for these laws.

The formula (3) was deduced on the hypothesis that a collision resulted in an ion being removed entirely from the original beam either by neutralization or deflection through a large angle. If the ions are deflected through small angles at a collision we have a more complex relation for the number removed from the bundle, which depends fundamentally on the size of the collecting chamber, that is, the angle through which an ion must be deflected to be removed from the beam. With any law of angular scattering at a collision we may theoretically deduce the weakening of the bundle to be expected in any particular apparatus. Let us consider an infinitely narrow bundle of rays *AB* which may be scattered by a gas during its passage through a distance x_1. We observe the number that enter a circular aperture of radius z_0, and the decrease in number as the first traces of gas are introduced. Assuming first the law of elastic collisions we see from Fig. 9 that the

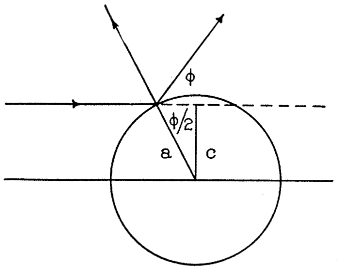

Fig. 9.

angle of deflection ϕ is connected with the sum of the two radii $a=(R_1 \times R_2)$ and the distance c by the relation $\cos(\phi/2)=c/a$. When gas is introduced gradually, the absorption at the lowest pressures must be due to single scattering from a beam of ions of almost constant strength.

In traversing a length of the path from $x+\Delta x$ to x the number making a collision such that c is between c and $c+\Delta c$ is $Qn2\pi c\Delta c\Delta x$ where Q is the number of ions in the beam and n is the number of molecules per cc. This number may be expressed in terms of ϕ by the relation $c=a\cos(\phi/2)$ giving $Qn2\pi\Delta xa \cos(\phi/2)\cdot(a/2)\sin(\phi/2)\Delta\phi$ and also in terms of z and x, since $\phi=\tan^{-1}(z/x)$. Thus

$$Qn2\pi\frac{a^2}{4}\Delta x\frac{z}{(z^2+x^2)^{1/2}}\;\frac{x}{x^2+z^2}\Delta z$$

is the number scattered to the ring between z and $z+\Delta z$. From the whole path, x_1, we obtain by integration over x, the number

$$Qn\frac{a^2}{4}\left[1-\frac{z}{(z^2+x_1^2)^{1/2}}\right]\Delta z\,.$$

The number scattered outside a circular opening z_0 is:

$$\begin{aligned}Q2\pi n\frac{a^2}{4}\int_{z_0}^{\infty}\left(1-\frac{z}{(z^2+x_1^2)^{1/2}}\right)dz&=Q2\pi n\frac{a^2}{4}\left[z-(z^2+x_1^2)^{1/2}\right]_z^{\infty}\\&=Q2\pi n\frac{a^2}{4}\left[(z_0^2+x_1^2)^{1/2}-z_0\right]\\&=Q2\pi n\frac{a^2}{4}\left(x_1\left[1+\frac{z_0^2}{x_1^2}\right]^{1/2}-z_0\right).\end{aligned}$$

In addition a number equal to $\frac{1}{2}Qna^2x_1$ is scattered at angles greater than 180°. Since n is proportional to the pressure, we have for small pressures $(1/Q)\,(\Delta Q/\Delta P)=-\text{constant}\,(2x_1-z_0)$. In general z_0 is small compared to x_1; in method II it was approximately 1.5 cm: 10 cm. We see that alterations in the opening of the collecting chamber have practically no effect on the rate of absorption observed. This is apparently the type of atomic force that comes into the absorption or scattering of slow electrons.

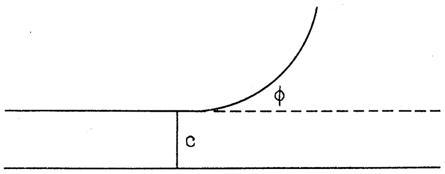

Fig. 10.

A different behavior is to be expected if a different law of atomic force is assumed. As an example, if the angle of deflection ϕ depends on the perpendicular distance c from the atom to the trajectory of the ion according to the law $\cot\phi = c/b$ for $c<(R_1+R_2)$ we may write the number scattered from a distance Δx at angle ϕ as before equal to $Qn2\pi c\Delta c\Delta x = Qn2\pi\Delta x\; b\cot\phi \cdot b\csc^2\phi\cdot\Delta\phi = Qn2\pi b^2\Delta x\cdot(x/2)\cdot(x^2+z^2)/z^2\cdot x\Delta z/(x^2+z^2)$. The number scattered from the whole path (0 to x_1), outside of a circular opening of radius z_0 is

$$Qn2\pi b^2x_1^3/3\int_{z_0}^{\infty}\Delta z/z^3 = Qn2\pi b^2x_1^3/6z_0^2\cdot$$

This gives an absorption equation for small pressures,

$$\frac{1}{Q}\,\frac{\Delta Q}{\Delta P} = -\text{constant}\cdot b^2\cdot\frac{1}{z_0^2}\cdot$$

For small values of ϕ the law of atomic scattering assumed above agrees with the inverse square law between the nuclei in which b is inversely proportional to the square of the velocity. If the law of force is of this type, we see that the rate of absorption observed is determined primarily by the aperture of the collecting chamber, z_0, and is also much less for high velocities than for low.

The present experiments show a strong dependence of the absorption observed on the aperture of the collecting chamber used and also a decrease of the absorption coefficient with high velocities, although not so rapid a decrease as would be required by the law of force just discussed.

Note added in proof. In the derivation of Eq. (13) it was assumed that all ions suffering single scattering were removed from the bundle. If however the absorption is due to small angle scattering, an ion may suffer more than one collision, depending on the ratio of the distance traversed x to the free path λ, and finally attain only a slight deviation from the original bundle. As the pressure is increased multiple scattering becomes important and a Gaussian distribution about the original bundle is finally established.[11] At the highest pressures used in these experiments x is less than 2.5λ[12], and the exponential decrease required by Eq. (1), continues to hold up to pressures of this magnitude, as is shown by the curve of Fig. 5.

The author remembers with pleasure the kindly interest of Professor A. J. Dempster during the experimental work and in the preparation of this paper.

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[11] Bothe, Zeits f. Physik **4**, 161, 300 (1921).

[12] See Fig. 6, curve marked I.