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of nitrogen atoms may occur:

$$N+N+M=N_2+M+7.35 \text{ ev.}$$

The metastable molecules have 6.14 ev energy of excitation, and active nitrogen is known to react with oxygen.[49] Further, there is the possibility of exchanges in ionization such as:

$$N_2^+ + CO = CO^+ + N_2 + 2.15 \text{ ev},$$

which may contribute to the initiation of the oxidation reactions. In a complex of products from an ionization process such as this it is obviously impossible to subject the system to a quantitative treatment. It is, however, quite evident that the addition of nitrogen to the carbon monoxide-oxygen system cannot fail to influence the velocity of the process as was actually found by Rosenblum.

[49] Wansborough-Jones, Proc. Roy. Soc. **A127**, 511 (1930).

The present analysis abundantly supports the point of view put forward by Eyring, Hirschfelder and Taylor in the ortho-parahydrogen conversion and the synthesis of hydrogen bromide as an explanation of alpha-particle reactions alternative to the older "cluster-theory." The preceding data indicate that the alternative is equally applicable to typical processes of alpha-particle decompositions, ozonization and oxidation processes. With increasingly available data on the primary products of ionization processes it may lead to satisfactory interpretation of all such processes.

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The scattering of slow electrons by gaseous molecules is discussed with the object of explaining the curves obtained when the apparent scattering area is plotted against a function of the electron velocity. The peaks frequently observed at about the ionization potential for most substances and the abnormally high values for the alkali metals are explained as being due to the formation or presence of positive ions. The rise in the curves for some substances, as the accelerating potential is diminished below the ionization potential, is explained as the result of an attractive force between the electron and the neutral molecule. It is shown that this attractive force for mercury approximates an inverse fourth-power law. From this law and an assumption of the diameter of the negative mercury ion, a reasonable value for the apparent electron affinity of mercury is calculated.

THE scattering of slow electrons in gases at low pressure has been studied by several investigators whose experiments have been summarized by Brode.[1] The effects are usually expressed in terms of α, the apparent cross section for scattering in square centimeters per cubic centimeter at 1 mm pressure and 0°C. Curves showing how α varies with the electron velocity show three distinct types. For argon, methane, etc., α is small for very slow electrons, increases to a maximum, and then decreases gradually as the electron speed increases. In some cases two or more maxima appear. For the alkali metals α at all electron speeds has a much greater value, and maxima and minima appear at lower electron velocities. Curves for the variation of α in zinc, cadmium, and mercury vapors show a very high value at the lowest electron speeds studied, a rapid falling off at higher velocities, and followed

[1] Brode, Rev. Mod. Phys. **5**, 257 (1933).

by a less marked maximum. Inspection of the curves seems to indicate a connection between the ionization potential of the molecule and the appearance of a maximum in the curve. The maximum is in many cases very near to the ionization potential, and with molecules of lower ionization potential the maxima appear at lower electron voltages. It is entirely reasonable to expect a maximum at about the ionization potential; for at this velocity of the electron, it has sufficient energy to produce positive ions. The positively charged particles thus formed would have a much greater scattering effect on the beam of electrons than neutral atoms or molecules and consequently a much greater apparent cross section. As the electron velocity increases above the ionization potential, its greater energy results in a smaller angle of deflection with the same scattering particles in its path, and a smaller apparent cross section results. At very high velocities the electron may approach close to the nuclei of the atoms with but a small deflection and the apparent cross section becomes less than the kinetic theory value. As the electron velocity is decreased below the ionization potential, the apparent cross section should decrease. However, should the neutral molecules exert a small attractive force on the electrons, a rise in α should be expected as the velocity is reduced to zero, for this force would produce a relatively large angle of deflection for low velocities. This is similar to the rise as the velocity is reduced from high values to the ionization potential.

The very high values reported for the apparent cross section of the alkali metals may be due to the positive ions present in the vapor. At the temperatures at which the experiments are performed thermal energy will cause some ionization. A variation of α with temperature should be found, if this explanation is correct.

Since α varies with electron speed in such a markedly different way for different substances, for example, argon on the one hand and mercury on the other, it is apparent that the interaction is different in the two cases. A study of the chemical properties of the two substances indicates the difference to be due to a much greater electron affinity, or ability to form a stable negative ion by addition of an electron, in the case of mercury. It is known that sodium and mercury react with

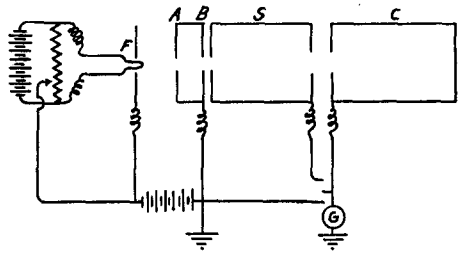

FIG. 1.

evolution of considerable energy, in which reaction the mercury presumably captures the valence electron of the sodium. Glockler[2] has calculated the electron affinity of mercury by an extrapolation method to be 1.8 electron volts. Quantitatively, the electron affinity is the energy consumed in removing to infinity an electron from a negative ion.

If energy is required to remove an electron from a negative ion, it would seem reasonable to assume that there is a force of attraction on an electron in the neighborhood of a neutral atom such as mercury that has the ability to form a stable negative ion. How this force of attraction would vary with the distance between electron and atom is, of course, unknown, but it may be assumed to vary as some inverse power of the distance.

It will be shown that the experimentally determined values of α for mercury are consistent with the assumption that the electron is attracted to the atom by a force varying as the inverse fourth power of the distance and that by assuming a value of the radius of the negative ion a reasonable numerical value for the electron affinity can be calculated. Because of the energy which would have to be dissipated in the formation of a negative ion, it is not likely that there will be actual attachment of electrons under the conditions of the experiments. Nor is this necessary to account for the scattering, since a force of attraction which simply deflects the electron somewhat from its path will cause it to be counted as scattered.

EXPERIMENTAL

A straight tube similar to that employed by T. J. Jones[3] was used. It is shown diagrammatically in Fig. 1.

[2] Glockler, Phys. Rev. **46**, 111 (1934).
[3] Jones, Phys. Rev. **32**, 464 (1928).

Electrons are drawn from the heated tungsten filament, F, and accelerated by varying positive potentials to A and B in the center of which are 2-mm holes. A and B are 1.5 cm apart. The electron beam thus produced passes through the scattering chamber S, 5 cm in length, with a hole at the further end 1.2 cm in diameter and into the collecting chamber C, 8 cm long. These chambers were 3.0 cm in diameter. The metal parts were nickel and enclosed in a Pyrex tube connected to a trap and the vacuum system. A galvanometer was used to measure the currents, connected by a switch so that either the current to the collecting chamber or the combined current to scattering chamber and collecting chamber could be measured. The currents were of the order of 10^{-7} ampere. Mercury vapor in the tube at known pressures was obtained by holding the trap at a given temperature. The pressures used varied from 2 to 20×10^{-4} mm. Reasonably straight lines were obtained by plotting the logarithm of the ratio of collector current to total current against the mercury vapor pressure. The values of α, the apparent cross section for scattering, were calculated from the equation,

$$\alpha=\frac{2.3}{l(p_2-p_1)}\log(R_1/R_2),$$

where l is the length of the scattering chamber, p_1 and p_2 the mercury vapor pressures in mm corrected to 0° and R_1 and R_2 the ratio of collector to total current at the pressures p_1 and p_2, respectively. The voltages corresponding to the velocity of the electrons passing through the scattering chamber were determined from graphs showing the relation of the current to the collecting chamber and opposing potentials applied to it. As is usual with this type of tube, a velocity spread amounting to a few tenths of a volt was indicated by the curves.

TABLE I.

Electron Velocity in Volts V	α_{Hg}	α_{Hg} Brode
2	260	230
4	157	150
6	123	100
8	93	77
10	79	64
12	63	56
14	59	51
16	58	50

In Table I are given the values of α obtained for mercury vapor and for comparison those reported by Brode.[4]

It will be noted that our values are somewhat higher than those of Brode. He states, however, that had he used the *International Critical Table* values of the vapor pressure of mercury, which were employed in our calculations, his values of α would have been increased by about ten percent. This would make the agreement good.

Discussion

The experimental values of α will be interpreted in terms of classical mechanics, assuming that the moving electron is attracted toward the atom center by a force varying as some inverse power, n, of the distance. From the known number of mercury atoms per cc in the scattering chamber and α, the effective cross section in square cm per cu. cm of space, the effective radius of a single atom to scattering may be calculated. Let this be r_0. An electron passing farther than r_0 from the atom center will not be sufficiently deflected to fail to get to the collecting chamber, while one which approaches within this distance will be sufficiently deflected. Hence the distance r_0, and therefore a definite value of α, corresponds to the average angle, θ, of deflection, which is just sufficient to make the electron miss the collector. This may be determined by the dimensions of the apparatus.

Since the mass of the atom is very great compared with that of the electron, and its motion at room temperature relatively slow, it will be considered at rest. The initial kinetic energy of the electron, V, is known and will be expressed in electron volts. The potential energy, P, of the electron owing to its attraction toward the atom is $-K/r^{n-1}$ where K is an unknown constant. Exact solution of the problem of the motion of the electron involves mathematical difficulties, but an approximate solution may be made as follows: For small angles of deflection

$$\tan\theta=CP/V, \qquad (1)$$

where θ is the angle of deflection, C is a constant,

[4] Brode, Proc. Roy. Soc. (London) **A125**, 134 (1929).

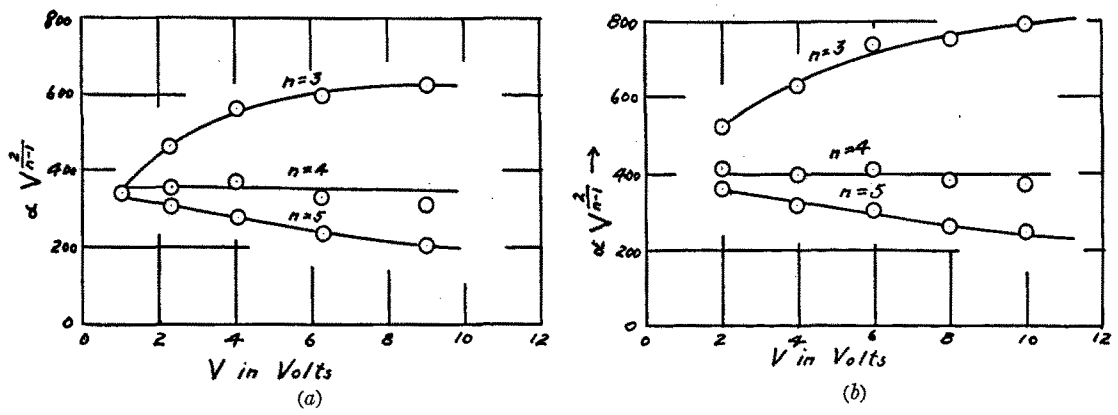

FIG. 2. (*a*) Calculated from results published by Brode. (*b*) Calculated from results of Simons and Seward.

P is the potential energy at the least distance r_0, and V is the initial kinetic energy. Inserting the previously mentioned energies—

$$\tan\theta = C\left(\frac{-K}{{r_0}^{n-1}}\right)\frac{1}{V},$$

r_0 and α are related by the equation $\alpha = \pi {r_0}^2 N$, where N is the number of atoms per cc;

hence $$r_0^2 = \alpha/\pi N$$

and $$r_0^{n-1} = (\alpha/\pi N)^{(n-1)/2};$$

substituting $$\tan\theta = \frac{C(-K)}{\alpha^{(n-1)/2}}\frac{(\pi N)^{(n-1)/2}}{V};$$

rearranging $$\alpha^{(n-1)/2}V = \frac{C(-K)(\pi N)^{(n-1)/2}}{\tan\theta},$$

all quantities on the right being constant:

$$\alpha^{(n-1)/2}V = k_1 \quad \text{or} \quad \alpha \cdot V^{2/(n-1)} = k_2,$$

which equation may be employed to find n.

Assuming an inverse 3-, 4-, and 5th-power force of attraction, the values in Table II have been calculated from the experimental values. Similarly using Brode's values, we obtain the values in Table III.

In both of these tables it may be seen that the product $\alpha V^{\frac{1}{2}}$, corresponding to inverse fourth-power attraction, is most nearly constant. Fig. 2 shows this graphically. Fig. 3 shows how a curve, based on the assumption that $\alpha V^{\frac{1}{2}}$ is constant, compares with the experimental points.

The relation between α, the initial energy of the electron, and the angle through which the electron must be deflected to be counted among those scattered, requires that, other things being equal, if the angle θ is increased α must decrease. It follows that a scattering chamber having a larger hole on the collector end should give a smaller value of α. In the Ramsauer type of apparatus used by Brode, the angle of deflection required for scattering is much smaller than that in the straight tube method. Hence the former should give larger α values. The experimental values cited indicate that the opposite is true. This was likewise found by Jones, who used both methods. It is not certain, however, that the two methods are strictly comparable. Experimental evidence contrary to the above-mentioned discrepancy is found in the work of Palmer[5] on the variation of α

TABLE II.

α	V	$V^{\frac{1}{2}}$	$V^{\frac{1}{3}}$	αV	$\alpha V^{\frac{1}{2}}$	$\alpha V^{\frac{1}{3}}$
260	2	1.59	1.41	520	413	362
157	4	2.53	2.00	628	397	314
123	6	3.31	2.46	738	407	302
93.0	8	4.00	2.84	745	372	267
79.2	10	4.65	3.16	790	368	250

TABLE III.

α	V	$V^{\frac{1}{2}}$	$V^{\frac{1}{3}}$	αV	$\alpha V^{\frac{1}{2}}$	$\alpha V^{\frac{1}{3}}$
340	1	1	1	340	340	340
205	2.25	1.72	1.5	462	353	308
150	4.00	2.53	2.0	560	379	280
95	6.25	3.40	2.5	594	325	238
70	9.00	4.34	3.0	630	304	210

[5] Palmer, Phys. Rev. **37**, 72 (1931).

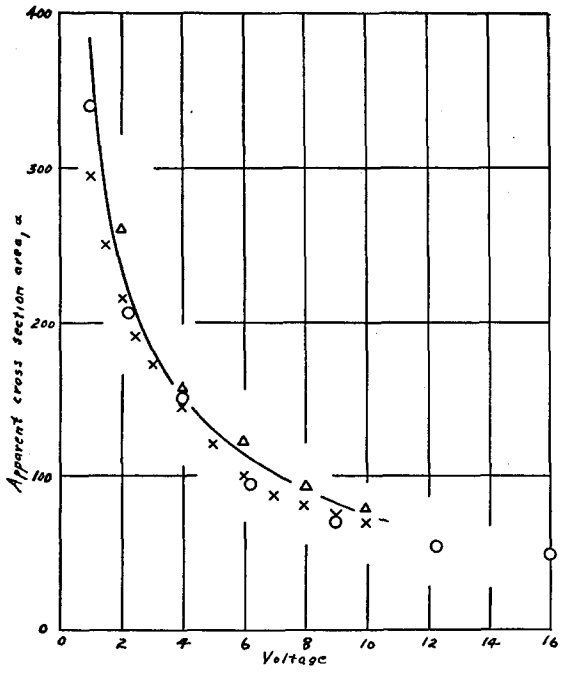

FIG. 3. Apparent cross-section area, α, of mercury at low voltages. The full line represents the theoretical fourth-power attraction. The points are from experiments of different investigators: O, Brode; ×, Jones, and △, Simon and Seward.

with the size of the aperture in the scattering chamber. A decrease in α with increase in aperture was found. However, Palmer did not use electrons below 20 volts, so his results can not be applied in the region discussed here. Experimental work on this point is planned.

The apparent electron affinity of mercury may now be calculated. For inverse fourth-power attraction the constant C of Eq. (1) is found following the method of Zwicky[6] to be -2.

$$\tan\theta = -2P/V = 2(K/r_0^3)(1/V).$$

$\alpha V^{\frac{2}{3}}$ has been previously found to equal approximately 400.

$$\alpha V^{\frac{2}{3}} = (2K/\tan\theta)^{\frac{2}{3}}\pi N = 400.$$

Solving this equation for K,

$$K = (400/\pi N)^{\frac{3}{2}} \tan\theta/2.$$

For the apparatus used the tangent of the average angle of deflection is 0.17 and substituting this and a numerical value of N:

$$K = \left(\frac{400\times 22.400\times 760}{3.14\times 6.06\times 10^{23}}\right)^{\frac{3}{2}} \frac{0.17}{2}$$

$$= 17.3\times 10^{-24}.$$

The potential energy of the electron in its equilibrium position in an ion will now be calculated. The radius of a negative mercury ion is not known. Presumably it would be larger than that of the negative iodide ion 2.16×10^{-8}, from crystal measurements. Assuming it to be 2.25×10^{-8} we find

$$P = -\frac{K}{r_i^3} = -\frac{17.3\times 10^{-24}}{(2.25\times 10^{-8})^3} = -1.53,$$

where r_1 is the ion radius.

The apparent electron affinity would be the negative of this or 1.53 electron volts. The uncertainty of the experimental values and the assumptions made preclude the possibility of an accurate value for the electron affinity, but this value seems to be a reasonable one. In the calculations it is assumed that the inverse fourth-power attraction holds down to the equilibrium position of the electron in the negative ion. This, of course, is not justified by the experimental data, since they are weighted in favor of those electrons which pass at large rather than small distances from the center of attraction. Theoretically, also, this law would be expected to change close to an atom or molecule. It may be argued that the total and not the potential energy of the atom-electron system is a measure of the electron affinity. Calculation of the total energy is uncertain however. Employing the virial theorem one obtains a positive total energy. This leads to the apparent absurdity of a negative electron affinity. On the other hand not enough is known of the quantum conditions obtaining in the interaction of an electron with a neutral atom or molecule to permit calculation of electron affinities.

Because of the uncertainties discussed above we have called the quantity which we calculated the *apparent* electron affinity. Although this may not be an accurate measure of the electron affinity it should be valuable, if only for the purpose of comparing the attraction which different atoms or molecules have for electrons.

[6] Zwicky, Physik. Zeits. **24**, 171 (1923).