EFFICIENCY OF EXCITATION BY ELECTRON IMPACT AND ANOMALOUS SCATTERING IN MERCURY VAPOR

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Abstract

The efficiency of excitation by electron impact of the 6.67 volt resonance level in the mercury atom has been studied as a function of the energy of the incident electrons. The electrons that have lost energy are separated out by a small retarding field and measured. The number of collisions is calculated from the experimentally determined value of the mean free path. The range covered is 0.4 volt from 6.67 to 7.07 giving a value for every 0.1 volt of the interval. The efficiency reaches a maximum of about 0.06 at 6.77 volts and then falls off to 0.04 at 7.0 volts.

The number of electrons scattered elastically at large angles by mercury vapor as a function of their energy was measured. The energy range covered was from 2 to 10 volts in steps of 0.2 of a volt. Certain very definite singularities were found. These correspond to an increase in large angle scattering and occur most prominently at 4.9, 5.7, and 6.3 volts. A less prominent group of singularities was also observed at 9.6, 10.3 and 11.1 volts.

Introduction

WHEN electrons travelling with a given velocity traverse a region occupied by a gas or vapor, two types of collisions can result. One type termed elastic collision refers to a process in which the electron on approaching the vicinity of an atom, suffers a change in direction but loses to the atom little or none of its energy. The other type known as an inelastic collision is characterized by the fact that the electron transfers to the atom all or nearly all of its energy. This transfer of energy can ionize or excite the atom. The necessary condition that an electron can suffer such a collision is that it have an energy greater than or equal to the ionization or excitation energy of the atom involved.

Franck and Einsporn[1] experimentally determined the critical potentials for electrons in mercury vapor. These critical potentials were exceptionally well checked in later work by Helen Messenger.[2]

Other experimenters have measured the absorption coefficient of mercury vapor for electrons as a function of the velocity of the electrons. This was done by Brode,[3] Maxwell,[4] and Jones.[5] These measurements necessitate the definition of a collision between an electron and an atom. The experiments were of two types. One defines a collision of an electron and an atom as any process that will remove an electron from the original beam by a change in

[1] Franck and Einsporn, Zeits. f. Physik **2,** 18 (1920).
[2] H. Messenger, Phys. Rev. **28,** 962 (1926).
[3] R. B. Brode, Proc. Roy. Soc. **109A,** 937 (1925).
[4] L. R. Maxwell, Proc. Nat. Acad. Sci. **12,** 509 (1926)
[5] T. J. Jones, Phys. Rev. **32,** 459 (1928).

direction. The other by nature of the experiment necessitates the removal of the electron from the beam if it suffers either a change in direction or a loss in energy. Both types of experiment give the same order of magnitude for the value of the absorption coefficient.

This presents another problem. If we take the values of the absorption coefficient (as experimentally determined in the work above) and calculate the fraction of the electrons that collide with atoms, what fraction (of the above fraction) lose energy when the electrons have a given velocity or energy? This may be called the efficiency of the process or, on the other hand, might be looked upon as the ratio of the collision area of the atom for excitation to the collision area of the atom as determined above from mean free path experiments.

Sponer[6] investigated the excitation of the mercury atom by electrons having velocities between 5 and 6 volts. She found an average efficiency for this range of 0.004. Hertz[7] recalculated her results taking a different value for the total number of collisions and obtained 0.03 for the average efficiency. These calculations were based on the kinetic theory value for the mean free path of the electron.

Eldridge[8] determined the relative probabilities of excitation of some of the important critical potentials in mercury vapor. He found evidence for loss in energy of the electrons corresponding to 4.9 volts as soon as the electrons have a velocity equivalent to 4.9 volts and that the efficiency of this process decreases as the velocity of the electrons is increased from this point on. He finds no evidence for a loss of energy of 6.7 volts when the incident electrons have energies corresponding to 6.7 volts but as the energy of the electrons increases the probability of excitation of 6.7 increases until it is quite pronounced.

Dymond[9] investigated the efficiency of excitation of the 19.77 volt level in the helium atom. He found that the efficiency increased to a maximum at about 0.25 of a volt above the critical potential and then decreased. The absolute magnitude of the maximum was found to be about one-tenth of one percent.

Glockler[10] has investigated the efficiency of excitation of the 19.77 volt level in helium by electron impact. He arrives at his conclusions by a study of the effect these inelastic collisions have on the current voltage characteristics of the experimental tube. He finds that the efficiency must rise to a maximum at about 0.2 of a volt after 19.77 and then falls off rapidly. He finds a maximum efficiency of 0.002.

This paper naturally divides itself into two parts. The first part is the description of an attempt by the writer to calculate the absolute efficiency of excitation by electron impact of the 6.7 volt energy level in the mercury

[6] H. Sponer, Zeits. f. Physik **7,** 185 (1921).
[7] G. Hertz, Zeits. f. Physik **32,** 298 (1925).
[8] Eldridge, Phys. Rev. **20,** 456 (1922).
[9] G. Dymond, Proc. Roy. Soc. London **107,** 291 (1925).
[10] G. Glockler, Phys. Rev. **33,** 175 (1929).

atom. The second part is the account of a study of the current-voltage characteristics of the tube and describes some conclusions arrived at as a result of this study.

Experimental Arrangement

The arrangement is shown diagrammatically in Fig. 1. Electrons from a hot tungsten filament were allowed to diffuse through the first diaphragm. They were accelerated by a given field between the first and second diaphragm. The third diaphragm was kept at the same potential as the second diaphragm. The electron beam defined by these diaphragms passed into the region inclosed by cylinders 1 and 2. The diameters of the diaphragms were 3 mm.

Some question was raised as to the possible effect of emission of secondary electrons from the walls of the first cylinder. The rings as shown were introduced to make cylinder 1 a better collector but this did not change the current-voltage characteristics of the tube thus indicating that the effect of such secondary emission was negligible.

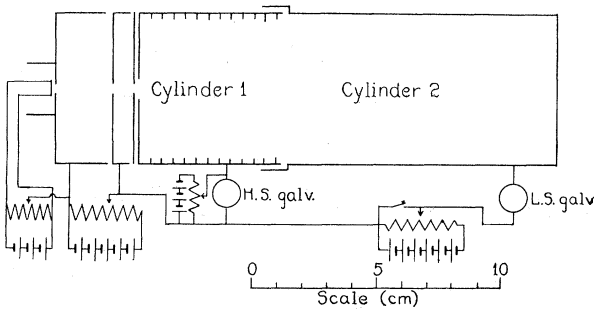

Fig. 1. Experimental arrangement.

Except for the filament, the tube was made of copper. The surfaces surrounding the diaphragms and the inside of the cylinders were coated with a thin layer of soot.

The arrangement was such that the electron stream was shielded from insulating surfaces on which charges might build up. All metal parts including the layer of soot were baked out to red heat under vacuum in an auxiliary vacuum furnace. They were then assembled in the final Pyrex tube where they were finally baked out at 500°C before the filament was lighted. Ground glass joints were used. They were covered on the outside by hard wax. The pressure inside could be maintained better than 10^{-4} mm of mercury for weeks at a time without running the pumps. Actually, when runs were taken the pumps were kept running. The tube was allowed to remain at room temperature and a mercury vapor trap was always kept at a temperature less than that of the room.

The earth's field was balanced out in the region occupied by the tube by the use of large Helmholtz coils.

It is to be noticed that the conditions under which this work was done were such that the mean free path of the electrons was of the same order of magnitude as the dimensions of the tube and that the current density was low. Total current was of the order of magnitude of 5×10^{-8} amperes.

These conditions are very different from the conditions generally present when critical potential measurements are made which are, high current density and short mean free path for the electrons.

Efficiency of Excitation

Let $f(v)dv$ be the fractional number of electrons having velocities between v and $v+dv$ where v is in volts. Let $\phi(v)$ be the chance that an electron having a velocity v will lose an amount of energy corresponding to a voltage drop of a if it collides with an atom. Let $C(v)$ be the fractional number of electrons that collide with atoms in a distance x when the electrons have a velocity corresponding to a voltage drop of v. Let $N(v)$ be the total number of electrons when the voltage drop is v. Then

$$n(v)dv=\phi(v)f(v)C(v)N(v)dv \tag{1}$$

where $n(v)dv$ is the total number of electrons that have lost energy in the interval v to $v+dv$.

Now if we can measure $n(v)\delta v$ the total number of electrons that have lost energy in the interval v to $v+\delta v$ where δv is a finite interval then we have

$$\phi(v)=\frac{n(v)\delta v}{N(v)f(v)C(v)\delta v} \tag{2}$$

where $\phi(v)$ is the average efficiency of excitation for the finite interval v to $v\pm\delta v$.

Now in order to determine the efficiency of excitation of the 6.67 volt energy level in the mercury atom we must measure the total current or the total effective number of electrons, the velocity distribution of the electrons, the number of collisions that these electrons make in a certain distance and the number of the electrons that lose 6.67 volts equivalent energy in this distance.

The experimental procedure was as follows: a galvanometer was connected to cylinder 2, and a very high sensitivity galvanometer was connected to cylinder 1. If we measure the current to cylinder 2 with retarding field and without retarding field at a particular voltage, the difference will give the number of electrons stopped by the retarding field. Also it does not matter whether we measure the change in the current to cylinder 2 or cylinder 1, as the geometry of the experimental arrangement is such that a decrease in current to cylinder 2 must be compensated by a corresponding increase to cylinder 1. Actually a high sensitivity galvanometer was connected to cylinder 1. The scattered current to cylinder 1 was balanced out by a counter e.m.f. across the galvanometer and only the difference in currents with retarding field on and off was measured.

Two runs were taken varying the accelerating voltage by steps of a tenth of a volt (Table I). At each value of the accelerating voltage, the current to the second cylinder was read, a reading on the high sensitivity galvanometer connected to cylinder 1 was taken, the retarding potential of a tenth of a volt was applied and the high sensitivity galvanometer was read again, the retarding potential was removed and the first reading on the high sensitivity galvanometer was checked. After this the accelerating voltage was moved up step by step, taking these readings at every step. Other runs were taken

TABLE I. *Sample data from runs 1 and 2 taken at a pressure of mercury vapor 0.0006 mm. V_a is the accelerating potential, i_t the total current, Δi_1 the difference between the current to cylinder 1 with and without the retarding potential of 0.1 volt, i_r the residual current, $C(v)$ the chance of collision.*

V_a	i_t	Δi_1	$\Delta i_1/i_t$ $\times 10^3$ run 1	$\Delta i_1/i_t$ $\times 10^3$ run 2	Ave. $\Delta i_1/i_t$ $\times 10^3$	i_r/i_t $\times 10^3$	Diff. $\times 10^3$	$\div C(v)$	Same $p=0.0014$ mm
4.1	364	0.6	1.65	2.32	1.98				
4.2	369	1.0	2.71	2.78	2.74				
4.3	375	1.0	2.67	2.48	2.57				
4.4	380	0.8	2.13	2.44	2.28				
4.5	386	0.7	1.81	2.40	2.10				
4.6	390	0.6	1.54	1.42	1.48	1.20	0.28	0.00131	0.00144
4.7	396	0.8	2.02	1.65	1.83	1.18	0.65	0.00305	0.00186
4.8	403	1.2	2.97	2.31	2.64	1.16	1.48	0.00686	0.00645
4.9	407	1.4	3.44	2.95	3.19	1.14	2.05	0.00964	0.00965
5.0	411	1.3	3.16	3.38	3.27	1.11	2.16	0.01015	0.01010
5.1	417	1.1	2.64	2.66	2.65	1.09	1.56	0.00733	0.00801
5.2	419	1.0	2.38	2.30	2.34	1.07	1.27	0.00597	0.00585
5.3	423	1.1	2.60	2.28	2.44	1.05	1.39	0.00653	0.00493
5.4	429	0.8	1.87	1.92	1.89	1.03	0.86	0.00404	0.00510
5.5	434	0.9	2.07	1.69	1.88	1.01	0.87	0.00408	0.00373
5.6	439	0.6	1.37	1.45	1.41	0.99	0.42	0.00197	0.00331
5.7	444	0.6	1.35	1.23	1.29	0.91	0.33	0.00155	0.00280
5.8	448	0.7	1.56	1.42	1.49				
5.9	453	0.6	1.33	1.61	1.47				
6.0	458	0.8	1.43	1.39	1.41				

from time to time, measuring the current to cylinder 2 and the total current to both cylinders. From these data, the total current can be computed for any other run, provided we know the current to cylinder 2. In the case of the two runs we are considering, the readings on the high sensitivity galvanometer were differenced, giving the current stopped by the retarding potential of a tenth of a volt.

The total current was computed and was multiplied by the ratio of sensitivity of the two galvanometers, and the current stopped by the retarding field was divided by this, giving the fraction of the total current stopped. These results for the two runs (taken on different days) were averaged and their plot against accelerating voltage is that given in Fig. 2. This process was then repeated for retarding fields of 0.2, 0.3, 0.4, 0.5 and 0.6 of a volt respectively. Two complete sets of runs were taken at pressures of mercury vapor corresponding to temperatures of 13°C and 22°C respectively.

The electrons stopped by the retarding field may be divided into two groups: first, electrons scattered elastically at large angles will be stopped if

their velocity component in the direction of the field, is too small to cross the retarding field; and second, some of the electrons that have lost energy in collision will be stopped by the retarding field. In Fig. 2 we have peaks superimposed on a residual current. The residual current is due to the first group, and the peaks to the second group.

In order to determine the energy loss to which each peak corresponds, we must know the voltage correction in the tube. By analyzing the peaks that occur in runs taken over a large range of accelerating voltages and by determining voltage at which ionization of the mercury vapor sets in, it was found that the voltage correction was approximately 1.8 volts. On this basis the second and largest peak in Fig. 2 is due to electrons that have lost 6.67 volts energy.

The number of electrons that, having lost energy, are subsequently stopped by the retarding field, will depend on three things; first, the direction

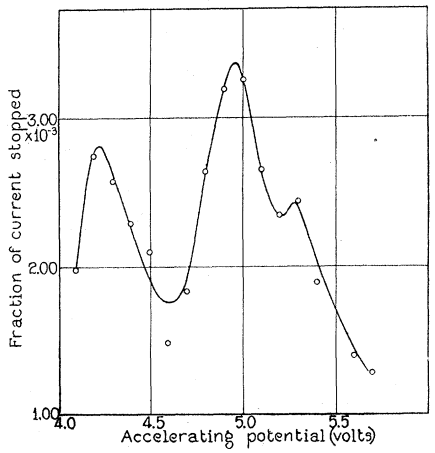

Fig. 2. Fraction of the total current stopped by a retarding potential of 0.1 volt. Mercury vapor pressure 0.0006 mm.

of their motion after inelastic collision; second, the amount of energy that they have left; and third, the potential difference between the second cylinder, and the point where the collision occurred.

For the purpose of this calculation, the writer feels justified in the assumption that the average angle of scattering on inelastic collision was small. No definite proof that this is so for the low velocities in this experiment was found, but indications from the study of current-voltage characteristics of the tube, pointed strongly to the fact that this assumption was correct. For instance, energy losses could be detected in the electron stream, entering cylinder 1 from the last diaphragm. The magnitude of these energy losses indicated that most of the electrons that lost energy while passing through the diaphragms continued straight on so as to come through the last diaphragm. On the basis of this assumption, it may then be said that the number of electrons stopped, over and above the residual current as

measured by the second peak for the case where the retarding potential was one-tenth of a volt, is a measure of the number of electrons that have lost energy, having a velocity to start with between 6.67 volts and 6.77 volts. (Fig. 2.)

In order to estimate the value of the residual current, runs similar to those described above were taken starting in at 2 volts and ending at 10 volts. From a plot of these results the residual current can be determined approximately and subtracted out. We then have left in Fig. 3 the electrons that

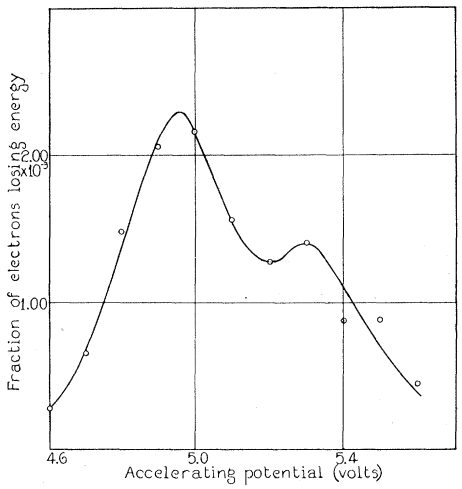

Fig. 3. Fraction of electrons that have lost energy due to inelastic collision, retarding field 0.1 volt, mercury vapor pressure 0.0006 mm.

have lost 6.7 volts energy when a retarding potential of 0.1 volt was applied.

Referring back to the theoretical development we now have

$$n(v)\delta v/N(v).$$

Now consider the two sets of runs for the two pressures of mercury vapor, 0.0014 and 0.0006 mm. If we knew $C(v)$ for both pressures we would have

$$\left[\frac{n(v)\delta)}{N(v)C(v)}\right]_{p_1} = \left[\frac{n(v)\delta v}{N(v)C(v)}\right]_{p_2}$$

where $C(v)$ is the fraction that have collided:

$$C(v) = I/I_0 = 1 - e^{-\alpha p x}$$

where x is the effective distance, α the effective cross section in cm^2/cm^3, and p the pressure in mm of mercury. We know p and from work of Jones,[5] Maxwell,[4] and Brode[3] α is approximately 100. This value is taken between 4 and 5 volts on Jones' curve. That this is the right point is shown by comparison of results in Jones' tube and the writer's tube.

The length of the first cylinder is 5.5 cm but there is good reason to doubt that this whole length is effective. To satisfy Eq. (3) it is necessary to take x

equal to 4 cm. This value of x was used as the approximate value of the effective distance. If we took 5 cm or 5.5 cm the results for the two pressures would not agree as well and the resulting efficiency would be decreased by a factor of 0.85 or 0.70 respectively.

Now that the choice of x is made the two sets of data can be corrected for pressure and corresponding curves averaged together. We then have a loss in energy curve for each value of the retarding potential.

The velocity distribution was determined by connecting cylinders 1 and 2 together and putting them at a negative potential of 6.67 volts with respect to the last diaphragm. The mercury vapor was frozen out with liquid air. The accelerating voltage was then varied in steps of a tenth of a volt measuring at each step the current to cylinders 1 and 2. The total current to cylinders 1 and 2 without retarding field was also measured at each step. The ratio of the current to the cylinders with retarding field applied to the total current gives the fractional number of electrons that had velocities great

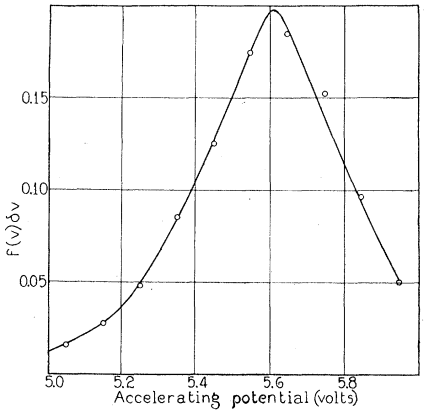

Fig. 4. Velocity distribution.

enough to cross the field. The plot of these values would give the integral of the velocity distribution. If we take the differences between successive values and divide by the interval (one-tenth volt) we have approximate values for the velocity distribution. If we do not divide by the interval we have $f(v)\delta v$ which is the quantity we wish to use in our calculations.

If we fit the values of $f(v)\delta v$ as shown in Fig. 4 to the values of $n(v)\delta v/N(v)C(v)$, as is done in Table II, and divide by corresponding values of $f(v)\delta v$ we get in each case a result for the average efficiency of excitation of 6.67 for electrons that had presumably velocities between 6.67 and 6.77 volts energy before colliding. Averaging these values we get an efficiency of 5.5 percent. The reason for considering only values of $n(v)\delta v/N(v)C(v)$ near the peak of the curve is that these are undoubtedly the most accurate.

Now in going on with the calculation we have two methods. One method would be to subtract from the curve for retarding potential $v_r = 0.2$ the curve for $v_r = 0.1$. This would introduce into the second calculation experimental

deviations in the first curve besides the experimental deviations already in the second. A second method would be to take 5.5 percent as the best value we have and, using the curve for $f(v)\delta v$, reconstruct the curve for $[n(v)\delta v/N(v)C(v)]$. The velocity distribution $f(v)\delta v$ is capable of fairly

TABLE II. *Completion of calculation for efficiency of excitation of the 6.67 level for electrons having velocities between 6.67 and 6.77.*

Accelerating voltage	Average of last two col Table I	Velocity distribution	Ratio	Average of ratio	Reconstructed curve
4.6	0.00137				0.0026
4.7	.00245				.0047
4.8	.00665	0.124	0.054		.0068
4.9	.00964	.173	.056		.0095
5.0	.01012	.184	.055		.0101
5.1	.00767	.152	.050	.055	.0084
5.2	.00591	.096	.062	——	.0053
5.3	.00573				.0028
5.4	.00457				.0017
5.5	.00390				
5.6	.00264				
5.7	.00217				

accurate determination. The second method appears to the writer to be the best. This procedure gives 5.5 percent as the efficiency of excitation of 6.67 by electrons having energies between 6.77 and 6.87 volts before they collided. Reconstructing again and proceeding in the same way, we get the values 4.8 and 4.1 percent respectively for electrons having energies between 6.87

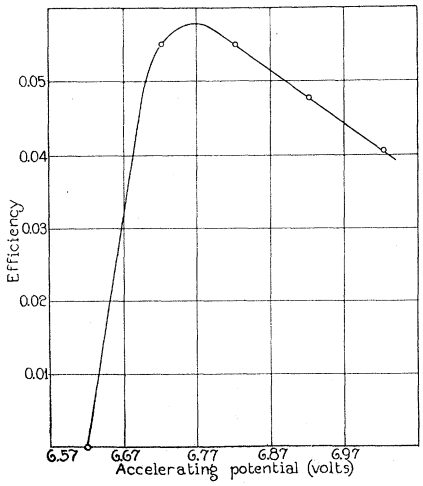

Fig. 5. Efficiency of excitation of the 6.67 volt energy level as a function of the velocity of the electrons.

and 6.97, and 6.97 and 7.07 before colliding. Carrying this procedure on to data obtained from retarding potentials of 0.5 and 0.6 volt meant very little, probably due to effect of another critical potential above 6.67. Fig. 5 shows these efficiencies plotted against accelerating voltage.

The position of the maximum of the curve for $f(v)\delta v$ on the accelerating voltage scale, Fig. 4, does not agree with the position of the maximum of $n(v)\delta v/N(v)C(v)$ in Fig. 3. The velocity distribution was determined by applying a retarding field between cylinders 1 and 2, connected together, and the electron gun. The ratio $n(v)\delta v/N(v)C(v)$ was obtained by applying a retarding field between cylinders 1 and 2. Measurement of critical potentials at both points showed a corresponding shift in the peaks. This is probably due to the action of a contact e.m.f. Therefore $f(v)\delta v$ was fitted to $n(v)\delta v/N(v)C(v)$ and moved up a tenth of a volt for each successive calculation.

As to the absolute value, this involves the choice of x and the direction the loss in energy electrons take after losing energy. If many electrons, after losing energy, are scattered at large angles, a drawing-out field on cylinder 2 should give some indication of this, and it does, but less than 25 percent of the effect with a retarding field. As for x, it cannot be much longer than 5 cm, which would mean a reduction of 15 percent, and if it were as short as 2 cm an increase of, roughly, 50 percent. A fair statement would be to say that the maximum average efficiency in any tenth volt interval near 6.7 was less than 20 and greater than 3 percent, and very probably between 5 and 15 percent.

It should be remarked that the present experiments have nothing to say about the efficiency of excitation of the 6.7 volt level by electrons having speeds in excess of that corresponding to about 7 volts. It is entirely possible, and studies of the intensity of 1849 in emission seem to indicate, that the efficiency of excitation of this level rises to a general maximum in the neighborhood of 15 volts. The present experiments merely indicate that this rise is not a smooth one but that there is at least one subsidiary maximum close to the critical potential.

Anomalous Scattering

From a study of the current arriving at cylinders 1 and 2 (both cylinders at the same potential) as a function of the accelerating voltage certain singularities or irregularities have been found.

On the basis of the fact that the mean free path of the electrons in mercury vapor increases with increasing accelerating voltage the fraction of the total current reaching cylinder 1 should fall off with increasing accelerating potential and the fraction of the total current reaching cylinder 2 should likewise increase. It would at first seem reasonable that this variation should be smooth and gradual.

It has been found that this is not entirely the case. Such curves as are shown in Fig. 6 are persistently obtained. This behavior might be due to a number of things besides the mercury vapor in the tube. To test this the mercury vapor was frozen out with liquid air. The curves obtained under this condition were always smooth. As a further test helium was introduced into the tube with liquid air still on the trap. In this case the curves were smooth in the region from 0 to 10 volts accelerating potential but in the

neighborhood of 20 volts singularities again appeared. It seems that this is very good proof that the singularities are a function of the gas in the tube.

Very little is known about the exact mechanism of the collisions between electrons and atoms as a function of the velocity of the electrons. Elasser[11] has calculated the absorption coefficient for slow electrons in atomic hydrogen up to and including the effect of the first resonance line. He finds an anomalous increase in the absorption coefficient at about the voltage corresponding to this resonance line. If he included other lines of the hydrogen spectrum in his calculations, might he not get other singularities?

Experimentally such singularities have been found by the writer in mercury vapor. In order to bring them out the high sensitivity galvanometer connected by cylinder 1 was used. The curve showing the variation of the current scattered to cylinder 1 as a function of the applied accelerating

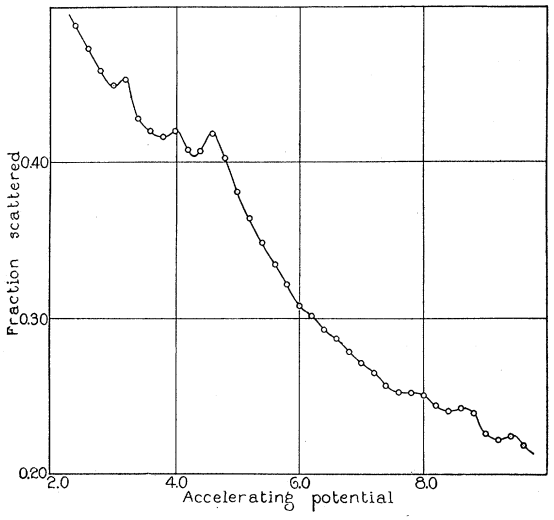

Fig. 6. Ratio of current scattered to cylinder 1 to the total current as a function of the speed of the electrons.

potential is shown in Fig. 6. The slope of this curve plotted on a voltage scale corrected for initial velocity is given in Fig. 7. It is an average of two separate runs that agreed very satisfactorily.

It should be pointed out that the singularities here observed are not due to inelastic collisions for these are relatively much too infrequent to produce the effects observed. The effects are due to rather abrupt increases, at certain critical potentials, of the number of electrons scattered by the mercury atoms through large angles. The relation of these potentials to the usual critical potentials of the mercury atom is uncertain. Excess scattering reaches a maximum at potentials (corrected) of 4.9, 5.7 and 6.3 volts; and again, though less pronounced, at 9.7, 10.3 and 11.1 volts. Between these two

[11] Elasser, Zeits. f. Physik **45,** 522 (1927).

groups are minor irregularities which are not prominent enough to allow one to attach to them much significance. It may be significant that there is a nearly constant difference of 4.8 volts between the corresponding maxima of the two groups.

It should be pointed out that the most prominent group of singularities accounts for the irregularity found in the mean free paths of electrons in

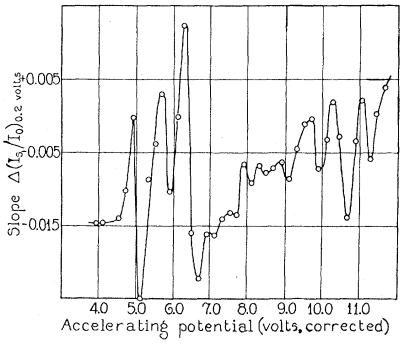

Fig. 7. Slope of the curve of Fig. 6.

mercury vapor by Maxwell[5] and Jones.[6] They are probably to be correlated with the maxima in the absorption coefficients for electrons in the vapors of the alkali metals which Brode[12] has recently found in the vicinity of the critical potentials of those metals.

In conclusion the writer wishes to express his appreciation for the advice of Professor John T. Tate under whose direction this work was carried out.

[12] Brode, Phys. Rev. **33,** 1069 (1929).