THE DIFFUSION OF METASTABLE ATOMS IN MERCURY VAPOR

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Abstract

The diffusion of metastable atoms in mercury vapor was studied with a four-electrode tube of special construction, and with short voltage pulses separated by variable time intervals actuating the accelerating and photo-electric gauzes. The change in the rate of arrival of metastable atoms at the outer boundary of a spherical volume of gas was determined as a function of the time elapsed after a number of atoms had been formed at the center. Observations were made at vapor pressures ranging from 3×10^{-9}mm to 0.33 mm. A comparison of the experimental results with the theoretical values for normal mercury atoms under the same conditions shows that the assumptions made by Webb and Messenger that metastable mercury atoms travel across the experimental tube and produce a direct action upon the "photo-electric" plate is correct. It is also found that the effective radius of the metastable mercury atom is about 1.5 times as large as that of the normal atom, and that metastable and normal mercury atoms obey the same general laws of diffusion. Evidence of the loss of energy of excitation as the result of collision between normal and metastable mercury atoms was found.

THE existence of metastable energy levels of the atom was first suggested for helium by Franck and Reiche[1] and is now well established. Several workers[2,3,4] have attempted measurements of the average life of the metastable state for mercury. Webb[5] found, by his alternating current method, that the average time of existence of the mercury atom in the metastable state for any temperature was proportional to the dimensions of the tube, i.e. to the distance through which the metastable atom would have to travel to reach the walls of the tube. He did not find, however, the expected increase in this time with the increase in the vapor pressure of the mercury. In his experiments advantage was taken of the fact that metastable mercury atoms free electrons from a nickel surface. Messenger[6] has confirmed this, and her results show that practically all the "photo-electric" current in a tube of the Lenard type with untreated nickel "photo-electric" plate is due to the metastable atoms or some other material body coming in direct contact with the "photo-electric" surface. The investigation described in this paper was undertaken to clear up the difficulty found in Webb's work, and to get more accurate information in regard to these bodies. The results confirm the assumption that these bodies are metastable atoms; for the sake of clearness they will be referred to as such throughout the discussion. A new method of studying the motion of these metastable

[1] Franck and Reiche, Zeits. f. Physik **1**, p. 154 (1920).
[2] Turner, Phys. Rev. **23**, p. 464 (1924).
[3] Marshall, Astrophys. J., **60**, p. 243 (1924).
[4] Gerlach and Schutz, Phys. Zeits., **26**, p. 33 (1925).
[5] Webb, Phys. Rev., **24**, p. 113 (1924).
[6] H. A. Messenger, Phys. Rev., **28**. p. 962 (1926).

atoms in mercury vapor was developed, which eliminated many of the complicated summations of effects which were necessary in Webb's work.

METHOD

The metastable atoms were produced and studied in a four-electrode tube, a cross-sectional diagram of which, drawn to scale, is shown in Fig. 1. Electrons emitted from a uni-potential hot cathode, *F*, were accelerated

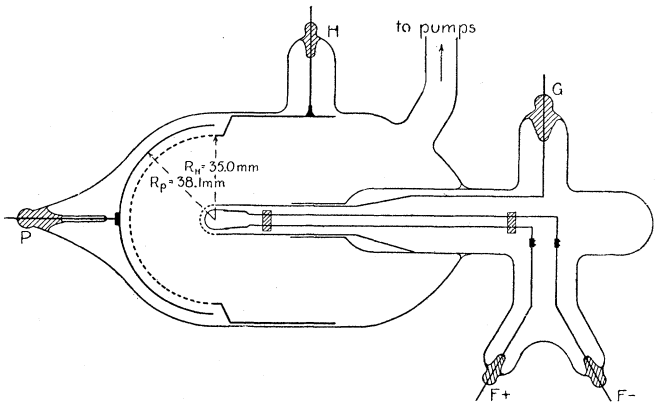

Fig. 1. Cross-sectional diagram of experimental tube.

by a potential difference applied between a hemispherical gauze, *G*, and the hot cathode. This *G-F* voltage consists of two parts: first, a constant potential difference just insufficient to produce metastable atoms; second, a voltage pulse of short duration, which we shall designate as the *G-F* pulse, superposed periodically on the constant potential difference. The metastable atoms were produced during the application of this *G-F* voltage pulse in the immediate vicinity of the gauze, *G*, and diffused through the volume of the gas to the detecting system, referred to as the "photo-electric" system, consisting of a nickel gauze, *H*, and a nickel plate, *P*. This "photo-electric" system has been shown by Messenger[6] to respond primarily to metastable atoms in a tube of this type with nickel surfaces. No electrons from the hot cathode could reach this system because of the voltage distribution on the electrodes. Between *H* and *P* a constant voltage was applied which, acting alone, gave no electrometer current; i.e. the average current to and from the plate due to electrons freed from the plate and the gauze by metastable

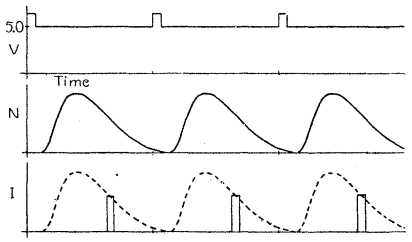

Fig. 2. Metastable atoms are produced during the *G-F* voltage pulse indicated in Graph V vs Time. The curve *N* vs Time indicates the rate of arrival of metastable atoms at the plate. The "photo-electric" current indicated in the curve I vs Time is a rectangular pulse, the peak value of which follows the dotted curve as the time interval between the *G-F* and *H-P* voltage pulses is varied.

atoms and radiation and due to currents resulting from leakage, etc., was zero. Therefore, when a voltage pulse of short duration was superposed on this constant *H-P* voltage, there resulted a current to the electrometer proportional to the quantity of metastable atoms reaching the "photo-electric" system during this pulse. It should be noted that some part of this current was due to the photo-electric effect of the radiation produced in the tube, but this was usually of negligible amount. By varying the time interval between the *G-H* voltage pulse and the *H-P* voltage pulse the rate of arrival of the metastable atoms at the wall formed by the "photo-electric" surface was determined as a function of the time elapsing since their production at the center of the tube. Fig. 2 illustrates graphically this method and shows the relation between the time of the production of the metastable atoms, their time of arrival at the wall, and the "photo-electric" current produced by them.

Apparatus

The experimental tube was designed to approximate spherical symmetry. The small oxide-coated platinum filament of the uni-potential type described by Webb[5] was located at the center of the sphere. The accelerating gauze, *G*, was a hemisphere of very fine platinum gauze welded over the end of a tube of sheet nickel, diameter 10 mm. The "photo-electric" gauze was a hemisphere of nickel gauze, 35.0 mm radius, mounted on a cylinder of sheet nickel which lined the walls of the glass tube. The "photo-electric" plate was a hemisphere, radius 38.0 mm, spun from a sheet of nickel. This plate was mounted rigidly on a nickel rod sealed into the end of the tube. The entire tube was enclosed in a box which could be maintained at the desired temperature. The system was evacuated by a mercury diffusion pump, pumping continually during observations. The pressure of residual gas was read with a McLeod gauge. Liquid mercury was present in the tube in order to keep the vapor pressure at saturation. The electrical circuits used to produce and apply the *G-F* and *H-P* voltage pulses are shown diagrammatically in Fig. 3. When the frequency of the voltage pulse was greater than 1000 per second a vacuum tube oscillator of the Hartley type, using a 7.5-watt Radiotron, UX-210, supplied the initial excitation wave for the pluse sets; for frequencies less than 1000 per second the oscillator was replaced by a specially constructed commutator. The excitation wave was applied across (see Fig. 3) two non-inductive resistances, R_1 and R_2, and a variable inductance, L_1, connected in series. By properly choosing the values of inductance and resistance in this combination, two voltage waves, differing in phase by 160°, were obtained. These two voltage waves were applied to the grids of the vacuum tubes 1 and 2, respectively. The grids of these tubes were biased so that plate current could flow only during the positive half cycle of the excitation wave. Consequently, the plate currents from the tubes 1 and 2 were half waves roughly rectangular in form. The plate currents from tubes 1 and 2 passed through the resistances, R_3 and R_4, respectively, and the resulting IR drops con-

trolled the grids of tubes 3 and 4 respectively. These two tubes gave plate currents more nearly rectangular in form, and differing in phase by 160°. The outputs of both tubes 3 and 4 were put through the resistance R_5, and the resulting IR drop blocked tube 5 completely except for the 20° interval during which no current was flowing through resistance R_5. The plate current from tube 5 was, therefore, a rectangular pulse existing during this 20° of the cycle. This 20° interval was sufficiently short to give the needed resolution. The plate current pulse from tube 5 passed through a non-inductive potentiometer, R_6, and the desired fraction of the resulting IR drop was applied to the experimental tube. The maximum value of L_1 was about 140 mh. The values of the non-inductive resistances R_1 and R_2 were 1500 ohms each, and the values of resistances R_3, R_4, R_5, and R_6 were 20,000 ohms each. The resistances R_7, R_8, and R_9, were 1/2 megohm grid

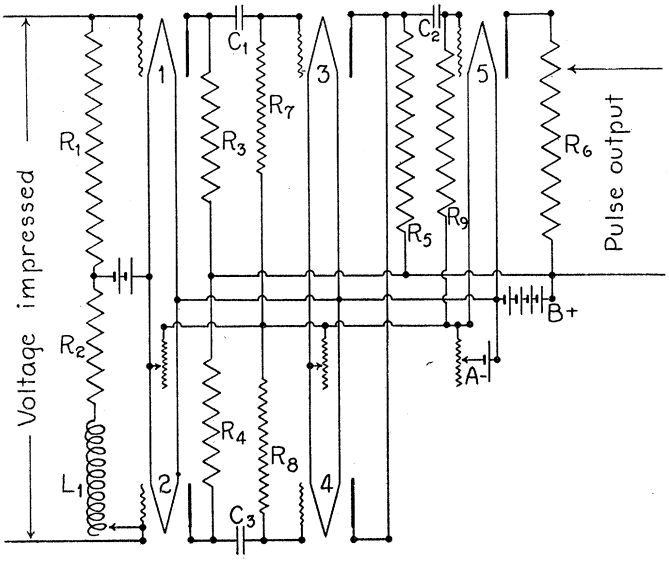

Fig. 3. Diagram of voltage pulse circuit.

leaks. The capacities C_1, C_2 and C_3 were 0.02 microfarad. The tubes 1, 2, 3 and 4 were Radiotrons, type 201-A, and tube 5 was a Western Electric 102-D.

Since all the resistances used were non-inductive the apparatus performed equally well for all frequencies used, when the proper adjustment of the inductance L_1 was made. The circuits diagrammed in Fig. 3 will hereafter be referred to as a voltage pulse set.

Two such voltage pulse sets were used, one for the production of the *G-F* voltage pulse, and another for the *H-P* voltage pulse. The two sets were exactly similar except that in the set for the *H-P* pulse the resistances R_1 and R_2 were 100,000 ohms each, and the inductance L_1 was replaced by a variable condenser. The variation of time interval between the application of the *G-H* pulse and *H-P* pulse was obtained by means of a phase shifting device placed between the exciting source and the *H-P* pulse set.

This phase shifting device consisted of a combination of inductance and resistance connected as shown in Fig. 4. The input wave passed through the inductance L_2 and the resistance R_p. L_2 and L_3 were "Duo-Lateral" coils of 1500 turns each, and R_p was chosen to make $2\pi Mf = R_p$, where f is frequency and M the mutual inductance between L_2 and L_3. The resistance of the output circuit i.e. R_1 and R_2 of the *H-P* pulse set, was made large (more than 200,000 ohms) so that the output e.m.f. consisted approximately of the two components—the IR drop in the resistance R_s and the induced e.m.f. in the coil L_3. By varying the mutual inductance and the resistance R_s simultaneously, it was possible to vary the phase of the output e.m.f. with respect to the input through 90° and the proper adjustment of the two reversing switches extended the possible variation through the full 360° of the cycle. It should be noted that R_p was adjusted for each frequency in order to make the maximum drop in the resistance equal to the maximum induced e.m.f. in the coil L_3. The device was readily calibrated by simple computation of the magnitudes of the values of RI and MdI/dt necessary to give the desired phase angles. These phase angles, as well as the wave form, were checked on a cathode ray oscillograph.

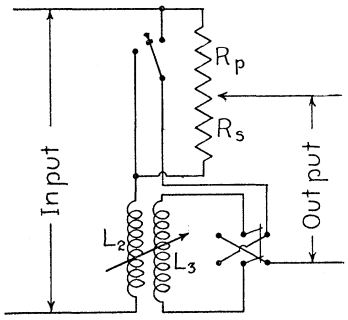

Fig. 4. Diagram of phase shifting circuit.

The special commutator was used to give the exciting voltage for the low frequencies where the values of inductance required by the Hartley circuit became inconveniently large. This commutator was run by a synchronous motor, and was arranged to control both the *G-F* and *H-P* pulse

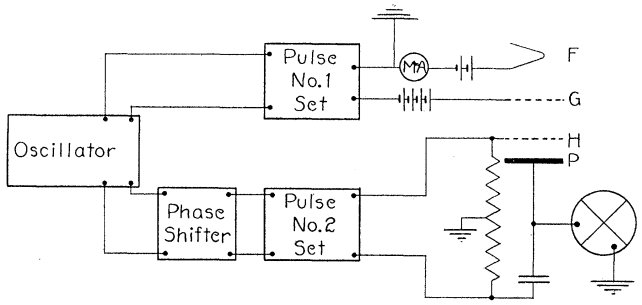

Fig. 5. Schematic diagram of connections to experimental tube.

sets. The two sets were controlled by identically constructed commutator discs mounted on a common axle. Each commutator disc was a bakelite wheel carrying on its periphery twenty-four carefully insulated brass segments. The alternate segments of the commutator disc were connected to a battery through a pair of slip rings in such a way that the device formed a high speed reversing switch. Hence, the voltage impressed on the pulse

sets was rectangular in wave form. The desired phase angle between the waves for the two pulse sets was obtained by rotating one commutator brush with respect to the other about the common axis.

Since the "photo-electric" gauze and plate of the experimental tube form a condenser in series with the electrometer, the application of a pulsating voltage to the gauze, *H*, resulted in a large deflection of the electrometer due to the induced charge. This was eliminated by making the "photo-electric" system one branch of a balanced capacity bridge, as shown in Fig. 5. When balanced, the electrometer deflected only for a current between the "photo-electric" gauze and plate. Fig. 5 shows schematically the complete set of circuits.

Procedure and Results

The procedure for making a set of observations consisted in adjusting the Hartley oscillator or the commutator to give a wave of known frequency, and observing the electrometer readings for various values of time interval between the *G-F* and the *H-P* pulses. A series of observations was made using various values of amplitude of the *G-F* pulse. The apparatus was not sufficiently sensitive to give satisfactory resolution in curves taken when using peak values of less than 5.6 volts (4.9 volts d.c and 0.7 volt pulse) for the *G-F* voltage pulse. Various values of this peak voltage gave curves that were identical in form. Hence measurements were made using values of peak voltage chosen to give electrometer readings within a convenient range. The curves obtained by plotting the time intervals versus the electrometer readings showed the variations in the rate of arrival of metastable atoms at the "photo-electric" plate with the time which had elapsed since their production.

The experimental results are illustrated by typical curves given in Figs. 6 to 9. Figure 6 gives the results for a mercury-vapor pressure in the experimental tube of 3×10^{-9} mm, mean free path 50,000 cm, temperature of the walls of the tube -80°C. Figure 7 gives results for vapor pressure of 5.4×10^{-4} mm, mean free path 13.5 cm, temperature of walls 10°C. Figure 8, Curve *B*, gives the results for vapor pressure 0.0013 mm, mean free path 5.7 cm, temperature of walls 20°C. Figure 8, Curve *C*, gives results for vapor pressure 0.0051 mm, mean free path 1.5 cm, temperature 37°C. Figure 9 gives results for vapor pressure 0.036 mm, mean free path 0.25 cm, temperature 65°C.

Discussion of Results

In studying these curves we must divide them into three groups: (a) those made at low temperatures at which the metastable atoms made a negligible number of collisions in traversing the tube: (b) those made at intermediate temperatures, at which the number of collisions made by any metastable atom in crossing the tube is small, a considerable number making no collisions: (c) those made at high temperatures, at which practically all metastable atoms made a number of collisions, and the laws of gaseous diffusion are expected to apply.

For Group (a), the dimensions of the vessel are very small in comparison with the mean free path, and the greater portion of the metastable atoms starting from the center of the vessel reached the walls without collision with other mercury atoms. When the metastable atoms start at the center of the spherical walls, their arrival is determined simply by the radius of the sphere and their speeds. With a Maxwellian distribution of velocities, the number having velocities between c and $c+dc$ is given by

$$4\pi N_0(hm/\pi)^{3/2}e^{-h\,mc^2}c^2dc$$

where N_0 is the total number starting, h a constant of kinetic theory, m the mass of atom. Hence the number N_t arriving during the interval between t and $t+dt$ is proportional to $(1/t^4)e^{-hmL^2/t^2}$, where D is the radius of the spherical wall.

When the mean free path of an atom is small in comparison with the dimensions of the sphere, (Group (c)), each metastable atom makes a large number of collisions with normal mercury atoms, and the rate of arrival at the wall is computed by the ordinary laws of diffusion of one gas in a second gas. For an approximate solution we consider the walls to form a closed sphere, near the center of which the metastable atoms are released during a negligibly short time interval. Assume the metastable atoms to be formed uniformly throughout a small sphere of radius a, and let the walls be a concentric sphere of radius b. The diffusion equation for the case of spherical symmetry is, if K be written for the diffusion constant of the metastable atoms in mercury vapor:

$$K\frac{\partial N}{\partial t}=\frac{\partial^2 N}{\partial r^2}+\frac{2}{r}\frac{\partial N}{\partial r}.$$

and assuming that metastable atoms become normal atoms on striking a metal wall (as shown by the results of Group (a), to be discussed later) the boundary conditions are: when $r=0$, N is finite, when $r=b$, $N=0$; when $t=0$, $N=f(r)=C$ (constant) for $r=0$ to $r=a$; and $N=f(r)=0$ for $r=a$ to $r=b$.

The solution is

$$\begin{aligned}N&=(\alpha r)^{-1/2}J_{1/2}(\alpha r)e^{-\alpha^2 t/K}\\&=(2/\pi)^{1/2}\sum A_\alpha(\alpha r)^{-1}\sin(\alpha r)e^{-\alpha^2 t/K}\\&=\sum(A_p/r)\sin(\alpha r)e^{-\alpha^2 t/K}\end{aligned}$$

where $A_p=(2/b)\int_0^a r\sin(p\pi r/b)\,dr$

Evaluating this integral we find

$$N=\frac{1}{r}\sum\frac{2b}{p^2\pi^2}\left\{\sin\frac{(p\pi a)}{b}-\frac{p\pi a}{b}\cos\frac{(p\pi a)}{b}\right\}\sin\frac{(p\pi r)}{b}e^{-Kp^2t\pi^2/b^2}$$

The rate of arrival of metastable atoms at the spherical boundary, C, is proportional to dN/dr for $r=b$.

Therefore

$$C=[\text{const}\,dN/dr]_{r=b}$$

and

$$C=(\text{const})\frac{1}{b}\sum\frac{2b}{p^2\pi^2}\left\{\sin\frac{(p\pi a)}{b}-\frac{p\pi a}{b}\cos\frac{(p\pi a)}{b}\right\}\frac{p\pi(-1)^p}{b}e^{-Kp^2\pi^2t/b}$$

The dimensions of the experimental apparatus are such that $a=0.63$ cm, and $b=3.80$ cm. Substituting these values we find the required relationship between the time interval between the G-F and H-P voltage pulses and the arrival of metastable atoms at the walls.

When the mean free path of the diffusing metastable atoms is of the same order of magnitude as the minimum possible path in the experimental tube (Group (b)) the theoretical treatment becomes very complicated. Some of the atoms cross the tube without making any collisions, while others make one or more collisions while travelling to the "photo-electric" plate. The fraction of the total number of atoms which have travelled a

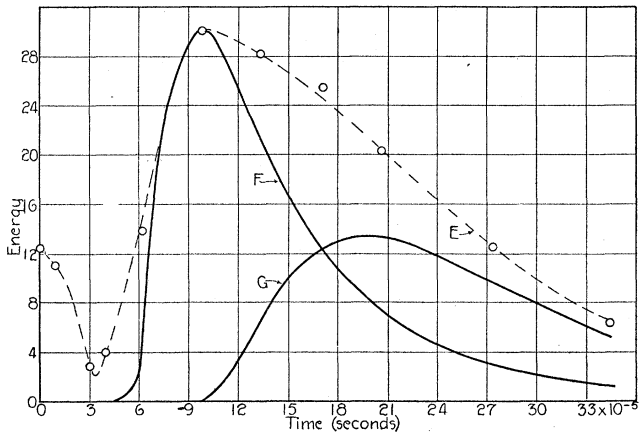

Fig. 6. Curve F gives theoretical arrival of metastable atoms travelling with Maxwellian velocity distribution for $T=770°$K. Curve G gives arrival of atoms travelling with Maxwellian velocity distribution for $T=193°$K. Curve E is the summation of Curves F and G.

distance greater than r since their last collision[7] is approximately e^{-r/λ_c} where λ_c is the mean free path of the metastable atoms. From this we may make an estimate of the percentage of the metastable atoms crossing without collisions. In the above relationship, two atoms are said to collide when they approach so that the distance between their centers is equal to the sum of their radii. This definition of a collision permits a very wide variation in the resulting path deflections.

The points plotted in Fig. 6 show how the metastable atoms arrived at the "photo-electric" plate with respect to time, when the walls of the tube were kept at the temperature of solid carbon dioxide (193°K). The small maximum in the curve at $t=0$ is due to radiation, probably $\lambda 2537$ as the "photo-electric" surface is slightly sensitive to this radiation. The persistance of this radiation is, however, in all cases so short that it has ceased to produce appreciable effect before the metastable atoms begin to reach the surface in appreciable number. The breadth of this radiation maximum in Fig. 6 is due, not to great persistance, but to the resolution

[7] Jeans, Dynamical Theory of Gases, p. 158.

of the apparatus. (The persistance of $\lambda 2537$ at this temperature is of the order of 10^{-7} seconds as determined by direct tests made in this laboratory but not yet published.) This maximum was present in all the experimental curves, but, since our primary interest is in the metastable atoms, it has been omitted from all other curves to avoid complication. The remainder of the curve is readily explained by assuming that 60% of the metastable atoms have a mean velocity corresponding to the temperature of the hot cathode, while 40% have a mean velocity corresponding to the temperature of the walls of the tube; the velocity of the metastable atoms being taken the same as for normal mercury atoms at the corresponding temperature. The temperature of the hot cathode was estimated from a rough comparison with an optical pyrometer to be about 770°K. Curve *F* shows the computed arrival of those atoms travelling with velocities having a Maxwellian distribution determined by the temperature of this hot cathode. Curve *G* shows the computed curve for the arrival of those atoms travelling with velocities determined by the temperature of the walls of the tube. The curve *E* is the summation of the curves *G* and *F*. It will be noted that the experimental points, shown by circles, fall very closely on the summation curve *E*. The close agreement here seems to show, first, that the metastable atoms and the normal mercury atoms have the same velocity distribution for a given temperature; second, that the metastable and the normal mercury atom have the same mass; and third, that the metastable atom changes to a normal atom immediately upon striking the metal walls of the vessel. The possibility of any considerable number of metastable atoms reflecting from the walls without losing their energy of excitation is eliminated, because such reflection at this vapor pressure would increase the average time interval between excitation and the delivery of the energy of excitation at the "photo-electric" plate by at least 1.5 times, and the curve indicates no considerable number of atoms arriving after such a lengthened time. Foote and Mohler[8] have suggested that an excited atom may combine with a normal atom to form an Hg_2 molecule. If the excited bodies arriving at the "photo-electric" plate were Hg_2 molecules, which dissociated upon arrival and delivered the excitation energy to the plate, the abscissae of the curve would be multiplied by the factor 1.4. We conclude, therefore, that we are dealing with metastable atoms at least in the case of this low pressure.

The experimental curve obtained when the walls of the tube were kept at 10°C is shown in Fig. 7. Curve *D* represents the computation for the time of arrival of those metastable atoms which cross the tube without making any collisions, assuming that 60% of these atoms have the same temperature as the hot cathode, and 40% have the same temperature as the walls of the tube. The ordinates of this curve are adjusted to fit the early part of the experimental curve as closely as possible. The difference between the experimental curve and Curve *D* is shown by Curve *C*. This curve, *C*, is approximately a Maxwellian velocity distribution, and is interpreted to represent the arrival of those metastable atoms which have undergone

[8] Foote and Mohler, Origin of Spectra, p. 106.

large deflections in crossing the tube. The number of collisions indicated by the area under Curve C is less than the number which would be predicted by the kinetic theory, because it does not include those atoms which were only slightly delayed in reaching the plate, as for example those atoms

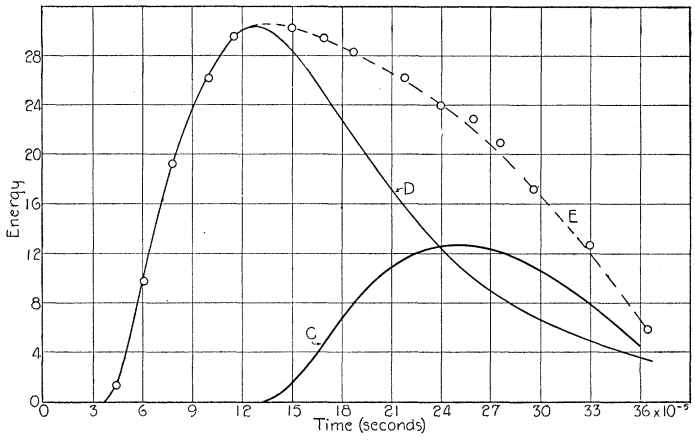

Fig. 7. Curve D gives the computed arrival of atoms crossing without collisions in gas at $T=283°K$. Curve E gives the experimental curve for gas at $T=283°K$. Curve C is the difference between Curves E and D.

which underwent only a small change in direction. The area under Curve D is 72% of the total area under the experimental curve. This gives us an upper limit for the number of metastable atoms crossing the tube without collision. The corresponding mean free path, λ_c, calculated from e^{-r/λ_c} fixes

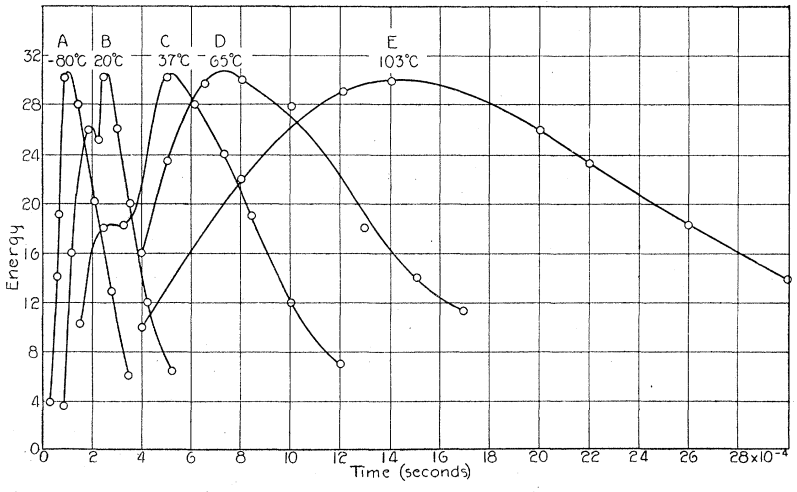

Fig. 8. Experimental curves for temperatures −80°C, 20°C, 37°C, 65°C and 103°C.

a lower limit for the effective diameter of the metastable atom which is 1.3 times the diameter of the normal mercury atom.

The curves B and C in Fig. 8 give the observations at 20°C and 37°C, and are typical of the range of pressure denoted as Group (b). The curves

A to E show graphically the transition from the range of low pressure represented by the curve for $-80°$C, Curve A, to the range of high pressure represented by the curves for 65°C, and 103°C, Curves D and E. No attempt has been made to compare the curves of Group (b) with theory quantitatively, because we do not understand the mechanism of the collisions sufficiently well. The general form of these curves indicates that the behavior is somewhat as we would expect, since the increase in the average time of arrival of the metastable atoms at the walls follows the increase in vapor pressure. The curves of this group indicate, in general, that some atoms cross the tube without making collision, while others make several collisions and are greatly delayed in arriving at the walls of the tube. Other curves taken in this intermediate range show even more marked complexity.

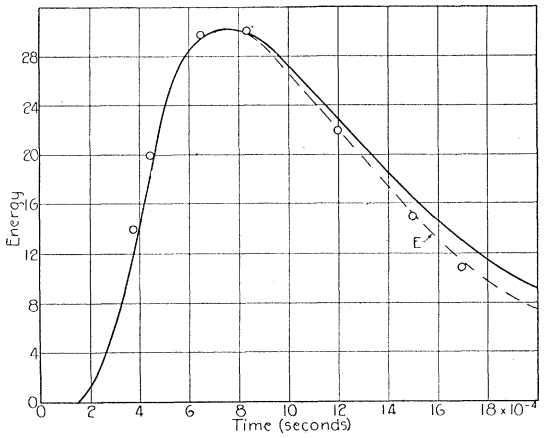

Fig. 9. Continuous line gives the computed curve for the arrival of diffusing metastable atoms when Diffusion Constant = 1700. Circles indicate observed values for temperature of gas 65°C.

For vapor pressures at which the diffusion process is the determining factor we get curves such as that shown in Fig. 9. The experimental curve E, (dotted) taken at 65°C, is in good agreement with the curve (solid line) computed from the diffusion equation given above. The value of the diffusion constant used in plotting the computed curve was chosen to give the best possible agreement with the experimental data.

Table I gives certain data for the curves discussed above. The temperatures used are listed in Column 1, and the corresponding number of atoms per cubic centimeter appears in Column 2. Column 3 shows the radius of the tube divided by the mean free path of the normal mercury atom, and Column 4 shows the same quantity for the metastable atom, assuming its diameter to be 1.5 times as large as that of the normal atom. For Groups (a) and (b), Columns 5 and 6 show the value of the quantity e^{-r/λ_c} (the fraction of the number of atoms crossing without collision) for the normal and metastable atoms, respectively. For Group (c), Column 5 shows the value of the diffusion constant D calculated from $D = 0.152/\nu\sigma^2(hm)^{1/2}$

TABLE I. *Data for curves of Figs.* 6, 7, 8, 9.

Temp.	Number of atoms per cc.	Radius of Tube ÷ mean free path: Normal Atom	Radius of Tube ÷ mean free path: Metastable Atom	e^{-r/λ_c}: Normal Atom	e^{-r/λ_c}: Metastable Atom
	Low temperature range. Group (a).				
−80°C	1.50×10^{8}	7×10^{-5}	1.6×10^{-4}	1.00	1.00
10°C	1.84×10^{13}	.26	.58	.79	.56
20°C	4.33×10^{13}	.61	1.37	.56	.26
	Intermediate temperature range. Group (b).				
27°C	7.6×10^{13}	1.07	2.4	.35	.09
37°C	1.6×10^{14}	2.30	5.2	.11	.005

Temp.	Number of atoms per cc.	Radius of Tube ÷ mean free path: Normal Atom	Radius of Tube ÷ mean free path: Metastable Atom	Diffusion Constant: Normal atom	Diffusion Constant: Metastable atom	Diffusion Constant: Experimental
	High temperature range. Group (c).					
65°C	1.05×10^{15}	15.2	34.2	2660	1930	1700
71°C	1.60×10^{15}	23.3	52.5	1760	1275	1190
103°C	8.43×10^{15}	121.	272.	351	253	750

given by Jeans[9] as the best value. Here ν is the number of atoms per cubic centimeter, σ is the diameter of the normal mercury atom, m is the mass of the atom, and h is a constant. Column 6 gives the values of the constant calculated for the interdiffusion of normal and metastable mercury atoms, when the diameter of the metastable atom is assumed to be 1.5 times as large as that of the normal atom, using the relationship $D_{12}=(c^2_1+c^2_2)^{1/2}/3\pi\nu S^2_{12}$. Here c_1 and c_2 are the mean velocities of the normal and metastable atoms, respectively, and S_{12} is the average of the diameters of the normal and metastable mercury atoms. Column 7 gives the values of the diffusion constant which were found by trial as best fitting the experimental curves, assuming only the processes of pure diffusion to be acting.

The value of the diffusion constant which best fits the experimental curve for 65°C is 1700. Substituting this value in the equation for D_{12} given above, the value of the effective diameter of the metastable atom is found to be 1.6 times that of the normal atom. The value of the diffusion constant which is best fitted to the experimental curve may, however, be too small, since the "photo-electric" plate was a hemisphere placed at the end of a cylindrical tube while the computation of the theoretical curve was made for a closed spherical volume. It is estimated that the error due to this fact is not more than 10%, which would accordingly reduce the estimated diameter. Taking 1.6 as the upper limit, and the value 1.3, determined from the 10°C curve, as the lower limit of the ratio of the diameters of the metastable and normal mercury atoms, we would estimate this ratio to be 1.5, which gives the effective diameter of the metastable mercury atom, 4.5×10^{-8} cm $\pm 0.5\times10^{-8}$ cm.

It is of interest to compare this estimate of the diameter of the metastable atom with the diameter of the excited mercury atom as determined

[9] Jeans, Dynamical Theory of Gases, p. 318.

from the quenching of resonance radiation and other methods. Stuart[10] estimates the diameter of the 2^3P_1 excited atom to be about three times as large as the normal atom, while Foote[11] estimates it to be 1.3 times as large. The experimental values of the diffusion constant, found above, again require the rejection of the idea that the excited body transferring energy to the "photo-electric" plate is an Hg_2 molecule, since the molecule having a mass and a radius each twice that of the normal atom would require a diffusion constant about 1/5 as large as the experimental values.

The experimental value of the diffusion constant for 103°C is 750. A comparison of this with the value 253 computed for the metastable atom having a diameter 1.5 times as large as that of the normal atom indicates that some process other than diffusion must be involved. Such a process may be collision of the second kind between the normal and metastable atoms, resulting in the destruction of the metastable state. An approximate calculation shows that a decay factor corresponding to one dissipative collision in 1300 will bring the computed curve into fair agreement with the experimental observations. This value of the dissipative factor is of the same order of magnitude as that found by Zemansky[12] in his work on the quenching of resonance radiation. Another possible process of dissipation of the energy of the metastable atoms is the formation, as the result of collisions, of Hg_2 molecules which strike the "photo-electric" plate without dissociation and without giving up their excitation energy to the plate. That this dissipation is not due to the presence of foreign gases seems certain, since throughout the experiment the tube was connected to the pumping system and the gauge showed less than 0.0001 mm residual gas pressure.

It appears that the failure of Webb[5] to find the expected variation in the time of diffusion with pressure was due to the form of the tube used (and perhaps in some degree to the dissipative action of foreign vapors arising from the greased joints in his experimental tube).

Summarizing the results discussed above we find that the metastable carrier of energy is a metastable mercury atom having a radius 1.5 ± 0.2 as large as that of the normal mercury atom. The velocity distribution at a given temperature is the same for the metastable atoms and the normal mercury atoms. A metastable atom loses its excitation energy immediately upon striking the metal walls of the tube. There is a strong indication of a dissipative process in which one collision in thirteen-hundred with normal mercury atoms results in the metastable atom losing its excitation energy.

In conclusion I wish to express my indebtedness to Professor H. W. Webb, at whose suggestion and under whose guidance this work was done. Thanks are also due to Dr. F. G. Slack and Dr. D. R. White for their assistance in checking the computations.

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[10] Stuart, Zeits. f. Physik **32**, 262 (1925).
[11] Foote, Phys. Rev. **30**, 288 (1927).
[12] Zemansky, Phys. Rev. **29**. 521 (1927).