RADII AND COLLISION PROBABILITIES OF METASTABLE NEON AND MERCURY ATOMS

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Abstract

The problem of the life-time of metastable atoms was treated on the basis of the assumptions that (1) metastable atoms diffuse to the walls of the containing vessel and give up their energy there, and (2) metastable atoms perform impacts with other atoms and are either lowered to the normal state or raised to a higher state. The result was obtained that, for large values of the time elapsing after the cut-off of the excitation, the average number of metastable atoms per cc decays exponentially with the time, with an exponential constant equal to $A/p+Bp$ where p is the pressure and A and B are constants containing the radius of the metastable atom and the probability of dissipative impact. The experimental results of Meissner and Graffunder, Eckstein, Zemansky and Pool are treated according to the theory, and values of the radius and probability are found. The radius in each case comes out smaller than the normal value, and the values of the probability are shown to substantiate the view that, in impacts between metastable atoms and either normal atoms of the same kind or foreign gas atoms whose first excitation potential is higher than the energy of the metastable atom, the metastable atom is raised to a state of higher energy.

IN A paper by Meissner and Graffunder[1] a critical survey is given of all the various methods that have been used to measure the lifetime of the neon atom in the metastable $^3P_2$ state, and new data are given that are the most reliable up to date. The method employed was briefly this: An absorption tube containing neon is electrically excited for a while, and then the excitation is cut off. After t seconds have elapsed, the absorption of the neon for $\lambda=6402$ $(2^3P_2-3^3D_3)$ is measured. (See Fig. 1a) Keeping the pressure of the neon constant and varying t, a curve is obtained where the ordinates represent percentage absorption, and the abscissas time in seconds. Curves of this character are given for neon pressures ranging from 0.50 mm to 5.60 mm. Since the degree to which $\lambda=6402$ is absorbed depends upon the number of atoms capable of absorbing it, the authors assume that

$$1-I/I_0 \propto N' \qquad (1)$$

where I_0 is the incident intensity of $\lambda=6402$, I the transmitted intensity of $\lambda=6402$, N' the average number of metastable 2^3P_2 neon atoms per cc traversed by the beam of light. The curves just described are therefore taken to represent the way in which the metastable neon atoms decrease with the time and the time necessary for the metastable neon atoms to decrease

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[1] K. W. Meissner and W. Graffunder, Ann. d. Physik **84**, 1009 (1927).

to one-half their original number is taken to be the lifetime of the metastable state at the particular pressure. It was found that the lifetime varied with the neon pressure, being a maximum at about 1 mm.

The experiment was performed with a cylindrical absorption tube of known dimensions, and consequently the number of absorbing metastable neon atoms could be computed approximately as a function of the time on the basis of the assumption that the decrease in the number of metastable neon atoms was due to two factors, namely, (1) diffusion to the walls, and (2) dissipative impacts with normal neon atoms. It was necessary to solve the

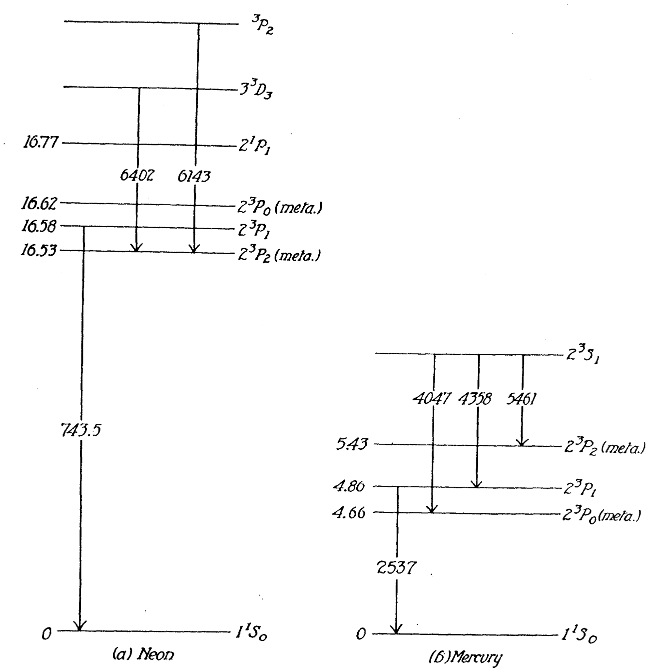

Fig. 1. Energy levels for neon and mercury. The lower metastable state is the one referred to in this paper.

diffusion equation for an infinite cylinder with a dissipative term in it, subject to the condition that, when $t=0$, the distribution of metastable atoms is uniform, and finally to integrate over a cylinder whose length is the length of the absorption tube, and whose radius is the radius of the light beam. The final result was expressed in the form of a series whose numerical value was found to depend very markedly on the ratio of the radius of the absorption tube to the radius of the absorbed light beam. Using a gas-kinetic value of the diffusion coefficient of neon, and assuming a probability of dissipative impact equal to 1.46×10^{-4}, the series was evaluated for various values of t, and the half-life was obtained for a number of pressures. The theoretical curve showing the relation between half-life and pressure did not agree well with the experimental one.

In view of the accuracy of Meissner and Graffunder's experiments, as well as the presence of reliable data on mercury, it was thought worth while to attack the general problem of the diffusion of metastable atoms in a way that would promise a better interpretation of existing experimental results in this field.

The Problem

Let us consider a cylindrical tube of length l and radius c placed with its center at the origin of cylindrical coordinates. Suppose that the tube is filled with a gas or vapor which either optically or electrically has been excited for a while, and that metastable atoms have been formed either in the presence of or without some foreign gas. Let the exitation be cut off and let a cylindrical beam of light of radius b which the metastable atoms are capable of absorbing traverse the tube.

We shall make the following assumptions:—(1) After the excitation is cut off, there is no further resultant rate of formation of metastable atoms. (2) Metastable atoms diffuse to the walls where they either become normal or are raised to a higher stationary state. (3) Metastable atoms perform impacts with normal atoms (and, if a foreign gas is present, with the molecules of the foreign gas, too) which either lower the metastable atoms to the normal state, or raise them to a higher state. (4) The rate at which metastable atoms are being raised to a higher state by the absorption of the light is negligible compared to the rate at which (2) and (3) go on.

The number of metastable atoms per cc, n will then be given by

$$\partial n/\partial t+kn=D(\partial^2 n/\partial r^2+\partial n/r\partial r+\partial^2 n/\partial x^2) \tag{2}$$

where D is the diffusion coefficient for metastable atoms and k is the number of dissipative impacts per second per metastable atom.

From kinetic theory:—

$$D=\frac{(3R\theta(1/m+1/M))^{1/2}}{3\pi\sigma^2 N}=\frac{\theta(3R\theta(1/m+1/M))^{1/2}}{3\pi\sigma^2\times 9.71\times 10^{18}p} \tag{3}$$

where R is Boltzmann's constant, θ the absolute temperature, m the mass of metastable atom in gm, M the mass in gm of atom of gas, p the pressure in mm, N the number of atoms per cc of gas and σ the distance between centers at impact in cm and

$$k=2\gamma\sigma^2 N\left[2\pi R\theta\left(\frac{1}{m}+\frac{1}{M}\right)\right]^{1/2}=2\gamma\sigma^2 p/\theta\times 9.71\times 10^{18}\left[2\pi R\theta\left(\frac{1}{m}+\frac{1}{M}\right)\right]^{1/2} \tag{4}$$

where γ is the probability that an impact shall raise or lower the metastable atom to a different stationary state.

It is necessary to solve Eq. (2) subject to the conditions that:

$$\text{at } t=0,\quad n=f(r,x) \qquad \text{at } t>0,\quad n=0\begin{cases}\text{at } x=-l/2\\ \text{at } x=+l/2.\end{cases}$$
$$\text{at } t>0,\quad n=0 \quad \text{at} \quad r=c$$

The solution is found to be:—

$$n=\sum_{\nu=1}^{\infty}A_{\nu}J_{0}\left(\frac{\mu_{\nu}}{c}r\right)\cos\left[\left(\frac{\beta_{\nu}-k}{D}-\frac{\mu_{\nu}^{2}}{c^{2}}\right)^{12/}\cdot x\right]e^{-\beta_{\nu}t} \tag{5}$$

where $\mu_{\nu}=\nu^{th}$ root of the equation $J_0(\mu)=0$,

$$\beta_{\nu}=\left[(2\nu-1)^{2}\frac{\pi^{2}}{l^{2}}+\frac{\mu_{\nu}^{2}}{c^{2}}\right]D+k \tag{6}$$

and the A's are such that

$$\sum_{\nu=1}^{\infty}A_{\nu}J_{0}\left(\frac{\mu_{\nu}}{c}r\right)\cos\left[(2\nu-1)\frac{\pi}{l}x\right]=f(r,x).$$

Let N' be the average number of metastable atoms per unit volume through which the beam of light has passed. Then

$$N'=\frac{1}{\pi b^{2}l}\int_{0}^{b}\int_{-l/2}^{+l/2}2\pi nr\,dr\,dx$$

$$=\sum_{\nu=1}^{\infty}C_{\nu}e^{-\beta_{\nu}t}$$

where the C's are constant coefficients.

From Eq. (6) we have

$$\beta_{1}=\left(\frac{\pi^{2}}{l^{2}}+\frac{5.81}{c^{2}}\right)D+k,\quad \beta_{2}=\left(9\frac{\pi^{2}}{l^{2}}+\frac{30.5}{c^{2}}\right)D+k,\qquad \text{etc.}$$

and consequently it is seen that, no matter what values l and c have, the exponential constants in the higher series terms increase very rapidly. If, therefore, we limit ourselves to large values of the time, we may discard all except the first term of the series, and obtain the result,

$$N'=C\,e^{-\beta t} \tag{7}$$

where

$$\beta=\left(\frac{\pi^{2}}{l^{2}}+\frac{5.81}{c^{2}}\right)D+k. \tag{8}$$

I. Neon

The experiments of Meissner and Graffunder give us the percentage absorption of $\lambda=6402$ as a function of the time for different neon pressures. If we adopt their attitude, as expressed by Eq. (1), then Eq. (7) tells us that the latter portions of the curves of $1-I/I_0$ against t ought to be exponential. Upon replotting these curves, this is found *not* to be the case. The reason is that Eq. (1) is not applicable to the experimental set-up of Meissner and Graffunder. They used a long narrow absorption tube, such as to warrant the use of the exponential law of absorption, namely

$$I = I_0 e^{-\alpha N' l} \tag{9}$$

where α is the atomic absorption coefficient of metastable neon atoms for $\lambda = 6402$, N' the average number of metastable neon atoms per cc traversed by the light beam, and l the length of the absorption tube. It is readily seen that Eqs. (1) and (9) agree for small values of $\alpha N' l$ but are quite different for large values. It is a simple matter to compute N' (in arbitrary units) from values of $1 - I/I_0$ on the basis of Eq. (9), and upon plotting the logarithm of these new values of N' against the time, the portions of the curves corresponding to $t > 2 \times 10^{-4}$ sec are all straight lines. The slopes of these straight lines give the exponential constants. The exponential constants are given in Table I.

TABLE I.

Neon pressure in mm	Exponential constant	Neon pressure in mm	Exponential constant
0.50	0.384×10^4	2.15	0.276×10^4
1.02	$.234 \times 10^4$	3.02	$.345 \times 10^4$
1.42	$.214 \times 10^4$	5.60	$.556 \times 10^4$

From Eqs. (3), (4) and (8),

$$\beta = \left(\frac{\pi^2}{l^2} + \frac{5.81}{c^2} \right) \frac{\theta (6R\theta/m)^{1/2}}{3\pi\sigma^2 \times 9.71 \times 10^{18}} \frac{1}{p} + \frac{4\gamma\sigma^2 (R\theta/m)^{1/2}}{\theta} \times 9.71 \times 10^{18} p.$$

In Meissner and Graffunder's experiments: $l = 12$ cm, $c = 1.8$ cm, $\theta =$ about 300°K, $m = 33.3 \times 10^{-24}$ gm and $R = 1.37 \times 10^{-16}$, whence

$$\beta = 5.15 \times 10^{-13}/\sigma^2 p + 8.00 \times 10^{21} \gamma \sigma^2 p. \tag{10}$$

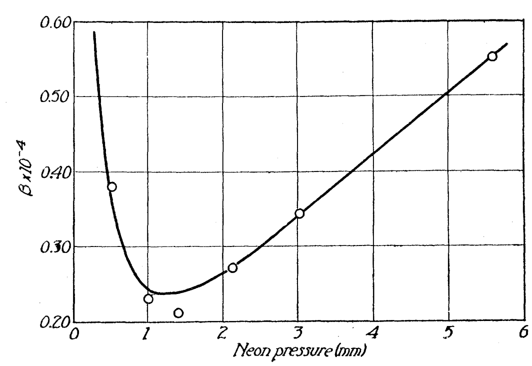

Fig. 2. Exponential constants of Table I as function of neon pressure. The curve is a plot of $\beta = 0.15 \times 10^4/p + 0.095 \times 10^4 p$.

In Fig. 2 the exponential constants of Table I are shown as points, and they are seen to lie quite well on the curve

$$\beta = 0.15 \times 10^4/p + 0.095 \times 10^4 p. \tag{11}$$

From Eqs. (10) and (11) we obtain: $\sigma = 1.85 \times 10^{-8}$ cm and $\gamma = 0.00035$.

From viscosity measurements, the radius of a normal neon atom is found to be 1.17×10^{-8} cm. Subtracting this value from the value of σ just found, we get for the radius of a metastable neon atom 0.68×10^{-8} cm, which is about 0.6 the normal value. This will be discussed later along with the interpretation of γ.

The recent work of Eckstein[2] provides a check on the experiments of Meissner and Graffunder. Eckstein measured the absorption of $\lambda=6402$ and $\lambda=6143$ (See Fig. 1a) in a cylindrical column of electrically excited neon in the steady state at various neon pressures and at constant current. Translating his values of percentage absorption into values of N' by means of Eq. (9) and plotting these values of N' against the neon pressure we get the dotted curve shown in Fig. 3. The circles represent the values obtained

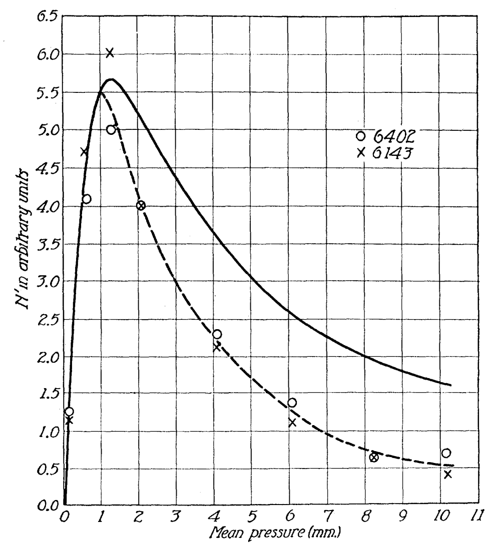

Fig. 3. Values of N' from Eckstein's measurements of absorption of λ6402 and λ6143 in neon. Dotted curve—experimental; full curve—Eq. (12).

by measuring the absorption of $\lambda=6402$ and the crosses refer to $\lambda=6143$ with the scale changed.

A theoretical expression can be obtained for the relation between N' and p on the basis of the same assumptions that were made in the beginning, except that, in place of assumption (1) we shall suppose that, in the steady state, with the current in the absorption tube constant, the rate of formation of metastable atoms is constant. Also, no appreciable error is introduced in regarding the absorption tube used by Eckstein as an infinite cylinder. We have, then, merely to solve the equation for the steady state

$$D(\partial^2 n/\partial r^2+\partial n/r\partial r)=kn-P$$

[2] L. Eckstein, Ann. d. Physik **87**, 1003 (1928).

where D and k have the same meaning as before and P is the constant rate of formation of metastable atoms. The boundary conditions are: when $r=c$, $n=0$, and when $r=0$, $n=$finite. The solution is found to be

$$n=\frac{P}{k}\left[1-\frac{J_0(i(k/D)^{1/2}r)}{J_0(i(k/D)^{1/2}c)}\right]$$

and the average number of metastable atoms per cc traversed by the light beam (which completely filled the absorption tube), N', is

$$N'=\frac{P}{k}\left[1-\frac{2}{c(k/D)^{1/2}}\;\frac{-iJ_1(ic(k/D)^{1/2})}{J_0(ic(k/D)^{1/2})}\right]. \tag{12}$$

Everything in Eq. (12) is known except P which we have assumed constant. D and k are obtained from Meissner and Graffunder's experiments and $c=1.8$ cm. Table II gives the numerical values. Eq. (12) is plotted in Fig. 3 as a heavy curve. It is seen that the agreement for small neon pressures is quite good. For large neon pressures where N' is approximately equal to P/k, the curve is too high, indicating that k in Eckstein's experiments is larger than in Meissner and Graffunder's. This is not surprising since the light beam, filling the absorption tube must have had an effect in removing metastable atoms comparable to the other effects. We shall regard, in what is to follow, that the values of k that fit Meissner and Graffunder's experiments represent a lower limit to the values of k that are correct for Eckstein's experiments.

TABLE II.

Pressure of neon in mm	D from M. & G.	k from M. & G.	N' (Arbitrary units) from absorption of 6402 and 6143	N' (Arbitrary units) from Eq. (12)
0.2	4060	190	1.60	1.30
0.3	2700	285	2.60	2.73
0.5	1620	475	3.85	3.80
0.7	1160	665	4.80	4.81
1.0	811	950	5.50	5.50
1.5	540	1430	5.00	5.57
2.0	406	1900	4.10	5.21
3.0	270	2850	3.05	4.28
5.0	162	4750	1.75	3.02
7.0	116	6650	1.00	2.27
10.0	81.1	9500	.50	1.67

If a foreign gas is present at a very low pressure then D remains unchanged but k is the sum of the k for neon alone and the k representing the number of dissipative impacts per sec per metastable neon atom with the foreign gas. If therefore, the pressure of the foreign gas is varied while the neon pressure remains constant, the new k will equal the old $k+k'p$ where $p=$pressure of foreign gas in mm, and

$$k'=2\gamma\sigma^2\times 9.71\times 10^{18}\left[2\pi R\theta\left(\frac{1}{m}+\frac{1}{M}\right)\right]^{1/2}\Big/\theta \tag{13}$$

We will have then

$$J=\frac{N'\text{ without foreign gas}}{N'\text{ with foreign gas}}$$

$$=\frac{\dfrac{P}{k}\left[1-\dfrac{2}{c(k/D)^{1/2}}\cdot\dfrac{-iJ_1[ic(k/D)^{1/2}]}{J_0[ic(k/D)^{1/2}]}\right]}{\dfrac{P}{k+k'p}\left[1-\dfrac{2}{c[(k+k'p)/D]^{1/2}}\cdot\dfrac{-iJ_1\{ic[(k+k'p)/D]^{1/2}\}}{J_0\{ic[(k+k'p)/D]^{1/2}\}}\right]}$$

and to a sufficient approximation at the neon pressures employed by Eckstein

$$J=1+k'p/k.$$

Table III gives Eckstein's results for a mixture of Ne and H_2, the neon pressure remaining constant at 2.18 mm.

TABLE III.

Pressure of H_2 in mm	% abs. of 6402	N'	J	% abs. of 6143	N'	J
0	61.4	4.14	1.00	48.3	2.85	1.00
1.4×10^{-3}	46.0	2.68	1.54	33.5	1.78	1.60
2.7×10^{-3}	17.9	0.86	4.81	12.2	0.56	5.09
3.7×10^{-3}	14.0	0.66	6.28	11.2	0.51	5.58
5.2×10^{-3}	10.0	0.46	9.00	8.7	0.40	7.13

In Fig. 4 J is plotted against the hydrogen pressure and a straight line is drawn. The slope yields a value of 1.37×10^3 for k'/k. Taking as a lower

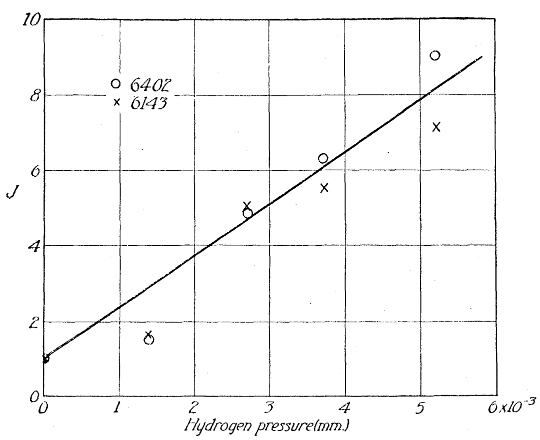

Fig. 4. Values of J as a function of pressure of hydrogen.

limit for k the value 2.07×10^3 obtained from Meissner and Graffunder's experiments for the neon pressure 2.18 mm, we get as a lower limit for k' the value 2.84×10^6, and finally, using Eq. (13), we get $\gamma=0.48$. It is quite likely that k in Eckstein's experiments is twice as large as in Meissner and Graffunder's and therefore it is possible that γ is unity, which would be expected in virtue of the large amount of energy that a metastable neon atom has compared with the small amount required by a hydrogen molecule for dissociation or excitation. Treating Eckstein's results for N_2 and He in the same way, we obtain, very approximately the values: γ for $N_2=0.06$ and for He, $\gamma=0.0002$.

II. Mercury Vapor

Several years ago the author performed a series of experiments[3] to determine the lifetime of the radiation imprisoned within a cylindrical mass of Hg vapor, and attempted to apply to the results the theory of the diffusion of imprisoned resonance radiation extended to include impacts of the second kind. The exponential constants which are given in Table IV were all very much larger than those calculated according to radiation diffusion and it was concluded that the discrepancy was due to absorption line broadening. Recently, experiments have been performed by Ramsauer[4] and Asada[5,6] which suggest a more satisfactory explanation of the results. According to these writers, metastable $^3P_0$ Hg atoms can give evidence of their presence by being raised to the excited $^3P_1$ state and then radiating $\lambda=2537$. (See Fig. 1b).

Table IV

No. of Hg atoms per cc $\times 10^{-15}$	Exponential constant $\beta\times 10^{-4}$ for large cell	$\beta\times 10^{-4}$ for small cell
0.77	2.66	
1.40	1.42	2.81
2.50	0.881	1.93
4.40	0.707	1.21
7.26	0.689	0.947
11.8	0.772	0.900
18.8	0.964	1.06
29.0	1.32	1.35

This was shown conclusively by the following experiment: Mercury vapor at the saturation pressure corresponding to room temperature was mixed with nitrogen at a few millimeters pressure and was excited for a while by $\lambda=2537$. The excitation was then cut off, and the persistence of 2537 was noted for almost 10^{-2} sec after the cut-off. This persistence can not be accounted for on the basis of the diffusion of the radiation, for on this basis the time [7] should be of the order of 10^{-6} sec. The only conclusion that can be drawn is that the metastable atoms which are known to be produced by impacts between excited Hg atoms and N_2 molecules decay partly by dif-

[3] M. W. Zemansky, Phys. Rev. **29**, 513 (1927).
[4] G. Ramsauer, Naturwiss. **16**, 576 (1928).
[5] T. Asada, Phys. Zeits. **29**, 708 (1928).
[6] T. Asada, R. Ladenburg, and W. Tietze, Phys. Zeits. **29**, 549 (1928).
[7] H. W. Webb and H. A. Messenger, Phys. Rev. **33**, 319 (1929).

fusing to the walls and partly by being raised to the $^3P_1$ level from which they either radiate 2537, or become metastable again. Asada, in a footnote suggests that this may be the explanation of the persistence of 2537 in pure Hg vapor at high vapor pressures. The author had arrived at this same conclusion before the papers of Ramsauer and Asada appeared, and the following is the result of the calculation with this point of view.

Since we are supposing now that the radiation emitted is proportional to to the number of times per sec that metastable Hg atoms are raised to the excited level, the radiation emitted should decay with the same exponential constant as the number of metastable atoms per cc. This exponential constant is given by Eq. (8). In these experiments, $l = 2.0$ cm for the large cell and 1.3 cm for the small cell; $c = 2.54$ cm; $\theta =$ about 350°K in the region where diffusion plays the main role, and about 390°K where impacts become important; $m = 331 \times 10^{-24}$ gm, whence, from Eq. (8), for the large cell

$$\beta = 3.4 \times 3.14 \times 10^3/\sigma^2 N + 9.04 + 10^4 \gamma \sigma^2 N \tag{13}$$

and for the small cell

$$= 6.8 \times 3.14 \times 10^3/\sigma^2 N + 9.04 \times 10^4 \gamma \sigma^2 N. \tag{14}$$

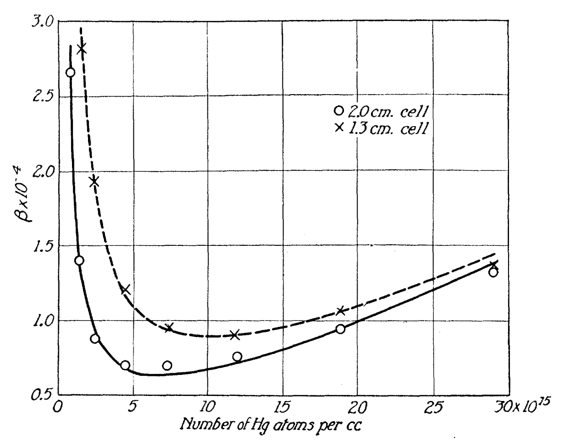

Fig. 5. Exponential constants of Table IV as function of mercury vapor pressure. Full curve—Eq. (15); dotted curve—Eq. (16).

Fig. 5 shows that the experimental points fit curves of this type very well, the points for the larger cell lying on the curve

$$= 2.0 \times 10^{19}/N + 4.6 \times 10^{-13} N \tag{15}$$

and those for the smaller cell, on the curve

$$= 4.0 \times 10^{19}/N + 4.6 \times 10^{-13} N. \tag{16}$$

From either Eqs. (13) and (15) or Eqs. (14) and (16), we get that $\sigma = 2.30 \times 10^{-8}$ cm and $\gamma = 0.0096$. Subtracting from σ the radius of the normal

Hg atom, 1.80×10^{-8} cm, we get, for the radius of the metastable Hg atom, 0.50×10^{-8} cm which is about 0.3 the normal value.

The diffusion of metastable Hg atoms through Hg vapor at different densities has been studied also by Coulliette.[8] He does not, however, give sufficient data to allow his curves to be treated by the methods of this paper. He found for σ the value 4.5×10^{-8} cm and for γ 0.00077. His value of σ yields a radius for the metastable Hg atom 1.5 times the normal value.

In a recent paper, Pool[9] measured the absorption of $\lambda=4047$ ($2^3P_0-2^3S_1$) in a cylindrical cell containing a mixture of mercury vapor at room temperature and nitrogen, as a function of the time elapsing after the excitation of the mercury vapor. The percentage absorption of 4047 gives the same information about the average number of metastable $^3P_0$ Hg atoms as the absorption of 6402 gives concerning the average number of metastable $^3P_2$ neon atoms, and in the same way. (See Fig. 1b). That is, using Eq. (9), Pool's values of $1-I/I_0$ enable us to obtain curves of N' against t for all nitrogen pressures. These were found to be exponential, and the exponential constants are given in Table V.

TABLE V.

Pressure of nitrogen (mm)	$\beta\times10^{-4}$	Pressure of nitrogen (mm)	$\beta\times10^{-4}$
2.5	0.791	16	0.364
4.8	.276	38	.545
6.8	.253	63	1.08
8.7	.274		

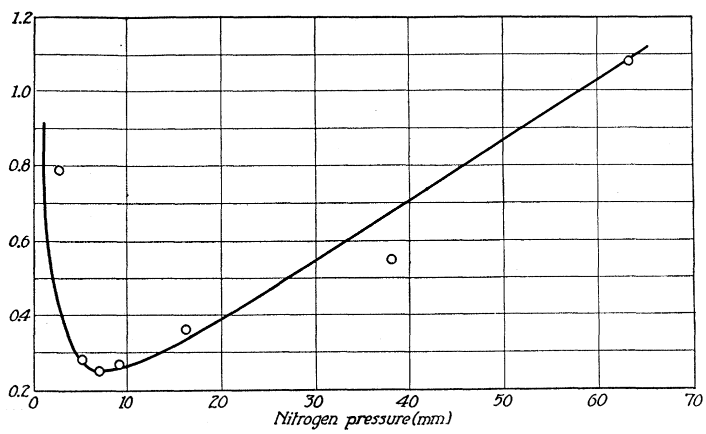

Fig. 6. Exponential constants of Table V as function of nitrogen pressure. Curve is a plot of $\beta=1.0\times10^4/p+0.017\times10^4p$.

In Fig. 6 the exponential constants are shown as points, and they are seen to lie fairly well on the curve

$$\beta=1.0\times10^4/p+0.017\times10^4p.$$

[8] J. H. Coulliette, Phys. Rev. **32**, 636 (1928).
[9] M. L. Pool, Phys. Rev. **33**, 22 (1929).

In Pool's experiments, $l=10$ cm, $c=0.75$ cm, $\theta=293°K$, $M=46.2\times10^{-24}$ gm (N_2), and $m=331\times10^{-24}$ gm (Hg). Substituting these values in Eq. (8), we get

$$\beta=1.81\times10^{-12}/\sigma^2p+0.522+10^{22}\gamma\sigma^2p$$

from which we get $\sigma=1.35\times10^{-8}$ cm and $\gamma=0.00018$. The value of 1.35 $\times10^{-8}$ cm for σ is astonishing since it is smaller than the gas-kinetic value of the radius of the nitrogen molecule, which is 1.58×10^{-8} cm.

The life of metastable Hg atoms was measured by Asada[6] by a very ingenious method, in which the emission of the green line 5461 was used to provide a measure for the rate at which metastable Hg atoms were raised from the $^3P_0$ level to the $^3S_1$ level by the absorption of 4047. (See Fig. 1b). The metastable Hg atoms were formed in a mixture of Hg vapor at room temperature and nitrogen at various pressures, and the life was found to depend on the nitrogen pressure. It has not been possible, as yet, to obtain the relation between exponential constant and N_2 pressure, and consequently σ and γ cannot be found. Asada's complete results will provide an interesting check on Pool's experiments.

Discussion

The results of all these calculations are collected in Table VI. Column three gives the value of σ calculated from the experimental data, and column four the value of σ obtained from viscosity measurements on normal atoms. The radius of the metastable atom, given in column five, is obtained by subtracting the radius of the normal atom from the experimentally determined value of σ. The most striking result that appears is that, in all cases but

Table VI.

Combination	Author	Exp. $\sigma\times10^8$	Normal $\sigma\times10^8$	Radius of met. atom $\times10^8$	γ	ϵ	Nearest energy difference
Ne Ne_m	Meissner and Graffunder	1.84	2.34	0.67	0.00035	0.26	0.24
H_2 Ne_m	Eckstein	1.76	2.26	.67	>.48		
N_2 Ne_m	Eckstein	2.25	2.75	.67	>.06		
He Ne_m	Eckstein	1.67	2.17	.67	>.0002	<.28	.24
Hg Hg_m	Zemansky	2.30	3.60	.50	.0096	.22	.20
Hg Hg_m	Coulliette	4.50	3.60	2.7	.00077	.31	.20
N_2 Hg_m	Pool	1.35	3.35	0	.00018	.28	.20

one, the radius of the metastable atom comes out less than its normal value. (Strictly speaking, Eckstein's experiments merely show that they are consistent with the value of σ found by Meissner and Graffunder). It is hard to say what this means. It is usually assumed that an atom has a larger radius in an excited state than in the normal state, and calculations of the radius of atoms in excited non-metastable states seem to verify this supposition. It is rather interesting, however, to note that the more refinements that are used in treating the experiments on the excited $^3P_1$ Hg atom, the smaller the radius is taken to be. For example, Stuart[10] assumed for this radius a value 3.4 times the normal, Foote[11], a value 1.2 times the normal and Gaviola[12] a value equal to the normal in some cases and larger than the normal in others. It is the opinion of the author that none of these values is reliable because the calculations that give rise to them are not refined enough to take account of the experimental conditions under which Stuart worked. There seems to be no reason *a priori* why an excited atom cannot have a radius smaller than the normal value, inasmuch as the whole conception of a radius is such an indefinite one. The value of σ yielded by Pool's experiments is very baffling. Perhaps it is connected with a sort of resonance between the $^3P_1$ and $^3P_0$ states of the Hg atom and the nitrogen molecule suggested by Cario and Franck[13] to account for the inability of nitrogen to quench Hg resonance radiation at high temperatures.

The values of γ are not quite as perplexing as the values of σ. In an impact between a metastable atom and a foreign gas molecule, the metastable atom may either give up some or all of its energy, or it may receive energy and be raised to a higher state. It is quite possible that in the case of impacts between metastable neon atoms and hydrogen and nitrogen, the metastable neon atom gives up some of its energy (16.5 volts) in dissociating the hydrogen and nitrogen molecules. Since the hydrogen molecule requires only 4.3 volts and the nitrogen molecule only 9.0 volts for dissociation, one would expect rather high impact probabilities. The values of 0.48 and 0.06 (these values being only lower limits) seem to corroborate this point of view.

On the other hand, when a metastable atom collides with a normal atom of the same kind, or with an atom whose first excitation potential is higher than the energy of the metastable atom, one would expect either nothing at all, or the lifting of the metastable atom to the next state of higher energy. On this basis γ ought to be equal to or less than that fraction of all the collisions in which the mutual kinetic energy is sufficient to raise the metastable atom to a higher level. Let ϵ represent this energy. Then, from kinetic theory

$$\gamma \lesseqgtr [(\epsilon/R\theta)+1]e^{-\epsilon/R\theta}.$$

In column seven of Table VI is given the value of ϵ corresponding to the value of γ in column six. It is seen that in the case of metastable Hg atoms the value of ϵ agrees fairly well with the difference in energy between the 2^3P_0 and 2^3P_1 states which is 0.20 volts. This is in agreement with the statement made before: that the persistence of 2537 in Hg vapor can be due to the raising of metastable 2^3P_0 atoms to the 2^3P_1 state and consequent radiation. A difficulty arises, however, in the case of metastable neon atoms dif-

[10] H. A. Stuart, Zeits. f. Physik **32**, 262 (1925).
[11] P. Foote, Phys. Rev. **30**, 288 (1927).
[12] E. Gaviola, Phys. Rev. **33**, 309 (1929).
[13] G. Cario and J. Franck, Zeits. f. Physik **37**, 619 (1926).

fusing through Ne and He. Here one would expect an impact probability corresponding to the difference in energy between the 2^3P_2 and 2^3P_1 states which is 0.05 volt. The experimental values of γ however, correspond to a much higher energy difference,—in the neighborhood of the energy difference between the 2^3P_2 and the 2^1P_1 states (0.24 volt). The only explanation of this that suggests itself is that perhaps when a metastable neon atom is raised to the 2^3P_1 or to the 2^3P_0 level it is not lost permanently. Since these two states lie so close to the 2^3P_2 state, neon atoms are probably going up and down among the states continually and in large numbers, and, although strictly speaking, this should be taken into account in the mathematical treatment, a crude way of looking at the state of affairs is to consider the rate at which metastable atoms are being raised to the 2^3P_1 and 2^3P_0 states equal to the rate at which they are entering the metastable level from these two states. On this point of view, the only way to get rid of a metastable atom is to raise it all the way to the $^1P_1$ state from which it radiates, before it can be knocked down.

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