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LIFE OF METASTABLE MERCURY AND EVIDENCE FOR A LONG-LIVED METASTABLE VIBRATING NITROGEN MOLECULE

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ABSTRACT

Curves showing the rate of decay of the metastable 2^3P_0 state of mercury atom in a quartz resonance cell, containing carefully purified nitrogen at room temperature, are not accurately exponential. The rate of decay in the neighborhood of 4×10^{-4} sec. after termination of the optical excitation, is more rapid than later. A high concentration of nitrogen molecules excited to the first and second vibrational states of the zero electronic state might be expected, due to collisions of the second kind between normal nitrogen molecules and mercury atoms in the 2^3P_1 or 2^3P_2 states. It is assumed that in addition to diffusion and dissipative impacts with unexcited nitrogen, the decay of the number of metastable mercury atoms may be influenced by dissipative impacts with these excited nitrogen molecules whose number decreases with time by diffusion and by dissipative impacts. An equation for the number of metastable mercury atoms is then obtained of the form $N=N_0\exp\left[-\alpha t+A(e^{-\beta t}-1)\right]$. Evaluation of the constants from experimental data gives the following: For excited vibrating metastable nitrogen molecule, maximum observed life 0.52×10^{-3} sec.; natural life, infinite; distance between centers at impact, 0.85×10^{-8} cm; probability of dissipative impact, 80×10^{-6}; diffusion coefficient 2.4 $\text{g}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}\cdot\text{dyne}^{-1}$. For the metastable mercury atom, maximum observed life, 2.54×10^{-3} sec.; natural life, infinite; distance between centers at impact, 3.2×10^{-8} cm; probability of dissipative impact, 3.3×10^{-6}; diffusion coefficient, 0.129 $\text{g}\cdot\text{cm}^{-2}\cdot\text{sec.}^{-1}\cdot\text{dyne}^{-1}$.

CERTAIN experiments on mercury fluorescence radiation with admixtures of hydrogen and nitrogen,[1] also iodine fluorescence radiation with admixture of helium,[2] and experiments on electron impacts in nitrogen,[3] have been interpreted[4] by assuming a strong persistence of molecular rotational and vibrational states in collisions. A recent treatment by Zener[5] based upon wave mechanics, of the interchange in internal energy of molecules during a collision has strengthened this contention that vibrational and rotational quantum numbers may have a marked reluctance to change. Furthermore, vibrational levels of the normal state of symmetrical molecules are strictly metastable. It was thought, therefore, that if the nitrogen molecule really persisted in a vibrational state for a long length of time, its influence upon the life of the metastable mercury atom might be detected experimentally, and an actual estimate of the life of the vibrating nitrogen molecule made.

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[1] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).
[2] J. Franck and R. W. Wood, Verh. d. D. phys. Ges. **13**, 78 (1911).
[3] W. Harries, Zeits. f. Physik **42**, 26 (1927).
[4] O. Oldenberg, Phys. Rev. **37**, 194 (1931).
[5] C. Zener, Phys. Rev. **37**, 556 (1931).

The life of the metastable mercury atom has been measured by various methods, but the method of interrupted optical excitation[6,7] seems to be the most simple and direct. This method as has been previously used indicates that the concentration of metastable atoms decays approximately exponentially with time. It is the purpose of this paper to show that the decay is found to be not accurately exponential when very pure nitrogen is used and great care is taken in the photometric measurements and that the departure from the exponential may be attributed to the persistence of the nitrogen molecule in excited vibrational states.

Apparatus and Method

Mercury vapor at the saturation pressure corresponding to 21°C and contained in a quartz resonance cell with various pressures of admixed nitrogen was excited optically by the total radiation from two 110 volt d. c. "Uviarc" quartz mercury arcs. The arcs were water cooled and the discharge pressed against the side of the quartz tube by a magnetic field. A strong air blast was also directed toward the anode of each arc. The position of the resonance cell with respect to the arcs is shown in Fig. 1. It is quite desirable to use two arcs for excitation instead of one, because in later considerations one wishes to assume a uniform concentration of metastable atoms in the resonance cell. But with only one arc it is not possible to get such a concentration, since the absorption coefficient[8] for the 2537 line in mercury vapor is approximately 3×10^{-14}; and therefore the greater number of metastable atoms would be produced within a few millimeters of the wall of the cell. This gradient in the

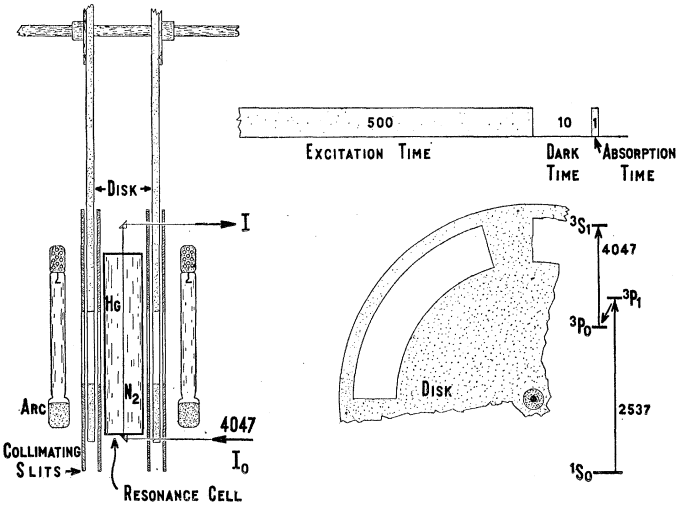

Fig. 1. Apparatus for intermittent optical excitation.

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[6] T. Asada, Physik Zeits. **29**, 549 (1928).

[7] M. L. Pool, Phys. Rev. **33**, 22 (1929).

[8] A. L. Hughes and A. R. Thomas, Phys. Rev. **30**, 466 (1927).

concentration of metastable mercury atoms along a diameter of the cell was noted by Wood[9] and roughly measured by Gaviola[10] in order to get an estimate of the life of the metastable state. However, with two arcs, one placed on either side of the resonance cell, there exists an overlapping of two gradients, giving in the center of the cell a region of comparatively uniform concentration.

The optical excitation of the resonance cell was interrupted by means of two disks, 50.4 cm in diameter and separated from each other by 3.5 cm. Between the disks was situated the resonance cell, 2.15 cm internal diameter and 12.4 cm long. In each disk were cut four sectors of such length that it was possible to excite the resonance cell 70 percent of the time per revolution of the disk. Collimating slits 1×55 mm were placed between the arcs and the resonance cell so that only 5.5 cm of the central portion of the cell would be excited and so that the excitation time would be sharply terminated whenever an opaque portion of the disk came between the arcs and resonance cell.

After the termination of the excitation period the cell remained dark for a short time until two one millimeter holes near the periphery of the disk came opposite two stationary ones. Then a flash of light from a glass 110 d. c. mercury arc, water cooled and magnetically deflected, passed longitudinally through the center of the resonance cell. Five small right angle prisms were used in directing this flash of light from one of the millimeter holes near the periphery through the resonance cell, and then through the other millimeter hole near the periphery. The light then passed through a lens before going into a spectrograph from which the slit was removed. The ratio of the time of flash to the dark time to the excitation time was 1 to 10 to 500.

A mercury diffusion pump slowly circulated the nitrogen through the resonance cell and over phosphorous pentoxide and hot copper and copper oxide for several hours previous to and during all runs in order to remove possible traces of hydrogen, oxygen, and water vapor. This method seemed quite effective because no HgO developed on the sides of the resonance cell even after 1000 hours of illumination. Eastman No. 36 plates were used. Each plate was calibrated with 15 to 20 density markings as obtained with neutral screens[11] mounted on eccentrics and placed between the spectrograph and the disk. A Moll self-recording microphotometer was used to densitometer the plates. Since the speed of the disk was varied over a range from 100 to 1000 r.p.m., the intermittency effect[12] was not constant and was found to vary several percent, depending upon the light intensity and the length of exposure.

RESULTS

For a mixture of nitrogen at a few millimeters pressure and mercury vapor at 21°C in the resonance cell, the mercury line 4047 ($2^3P_0-2^3S_1$) always showed marked absorption in the neighborhood of 10^{-4} sec. after the interrup-

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[9] R. W. Wood, Phil. Mag. **4,** 466 (1927).

[10] E. Gaviola, Phil. Mag. **6,** 1167 (1928).

[11] G. R. Harrison, J.O.S.A. and R.S.I. **18,** 492 (1929).

[12] C. E. Weinland, J.O.S.A. and R.S.I. **15,** 337 (1927).

tion of the optical excitation. The lines 3650, 4077, 4358, 5461, 5770 and 5790 showed at no time any measureable absorption. An investigation of the amount of absorption of 4047 was made for various time-waits (i.e. for various lengths of the dark period previous to the passage of the flash of light) in order to obtain a measure of the concentration of the metastable 2^3P_0 state. However, the amount of absorption is not directly proportional to the concentration because of the atomic absorption coefficient, μ, defined by $N=N_0 \mu^{-1}\log(I_0/I)$, where N is the number of metastable atoms per cc, I_0 is the intensity of 4047 after passing through previously unexcited resonance cell and I is the intensity after passing through previously excited cell.

The general nature of the rate of decay of absorption with respect to increased time-wait after termination of optical excitation is shown in Fig. 2.

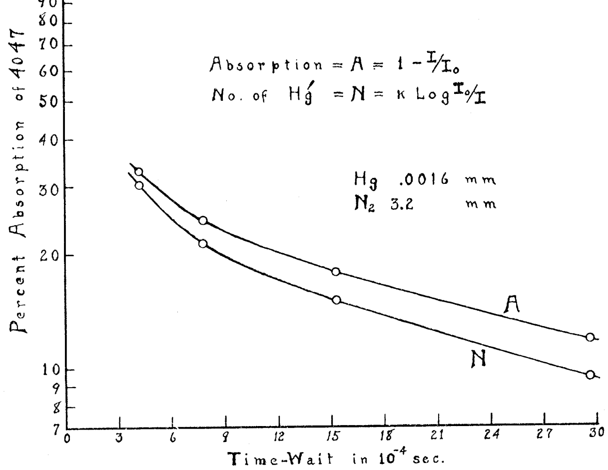

Fig. 2. A, semi-logarithmic plot of percent absorption of 4047 in mercury vapor with 3.2 mm pressure of admixed nitrogen against the time after termination of optical excitation. N, semi-logarithmic plot of the corresponding number of metastable mercury atoms in arbitrary units.

It may be noted that after 3×10^{-3} sec. there still exists over 11 percent absorption. As shown in the figure the effect of the absorption coefficient is to give a decay rate of N somewhat greater than the decay rate of the absorption of 4047. The most important point however, in this figure, is that the N curve is not a straight line but concave upward, indicating that the metastable states decay more rapidly at first and more slowly later. This same character is evident for other pressures as shown in Fig. 3. For nitrogen pressures below 2 mm (not shown in Fig. 3) the curves are straight lines whose negative slope increases with decrease in pressure. Above 2 mm the curves are concave upward with an average negative slope that decreases until a pressure of 5 mm is reached. Beyond 5 mm the average negative slope increases with increased pressure. No measurements were made beyond 50 mm nitrogen pressure.

Two objections might be made against the reality of $dN/dt \neq$ constant as expressed by the fact that the curves of Fig. 3 depart from a straight line. First, N as obtained through the percent absorption and absorption coefficient may not be directly proportional to the number of Hg$'$ (metastable 2^3P_0 mercury atoms) per cc, because of various factors; namely, absorption coefficient changing[13] with number of Hg$'$, pressure broadening of absorption line, displacement and dissymmetry in form of absorption line due to admixed foreign gas.[14] In order to test this possible objection, the emission of 2537 was obtained at various time-waits after termination of the optical excitation. It is generally agreed that the intensity of 2537 at any particular instant after optical excitation is directly proportional to the number of metastable 2^3P_0 atoms present at that particular instant provided the concentration of the 2^3P_2 atoms is negligible, which is the case for mercury and nitrogen admixtures as will be pointed out later. Fig. 4 shows the values of the intensity of the emission of 2537 in arbitrary units and also the values of N as obtained from the absorption of 4047 plotted on semi-log paper against the time-wait in 10^{-4} sec. It is seen that the two are in fairly good agreement. It must be, therefore, concluded that the various factors mentioned above change but little when the partial pressure of Hg$'$ alone changes. One must not, however, conclude that these factors remain constant when the nitrogen pressure is changed. The advantage of running absorption measurements of 4047 in-

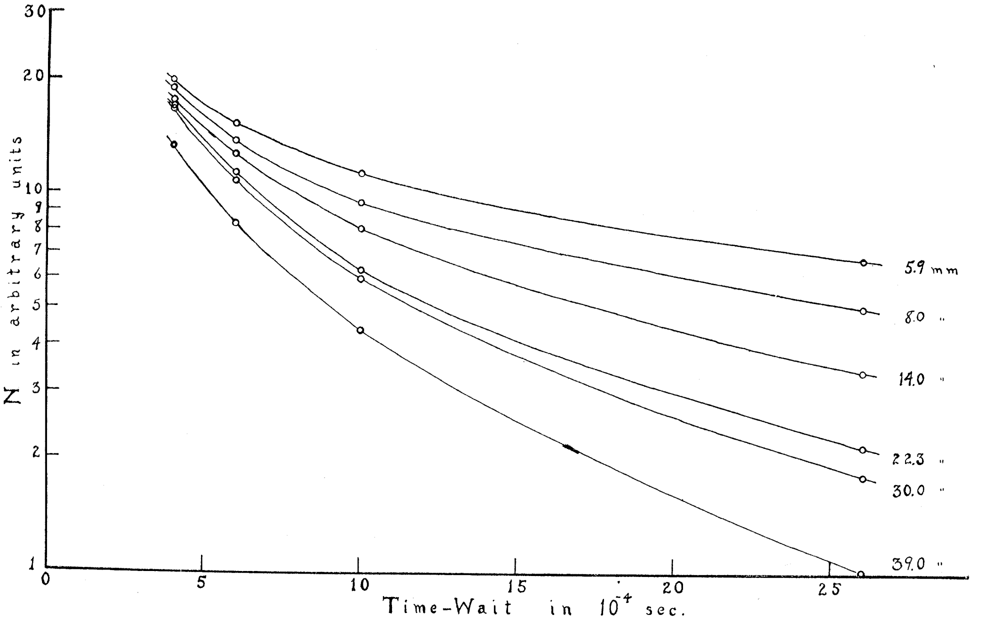

Fig. 3. Semi-logarithmic plot of the number of metastable mercury atoms in arbitrary units for various nitrogen pressures against the time after termination of optical excitation.

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[13] A. R. Thomas, Phys. Rev. **35**, 1253 (1930).

[14] P. Kunze, Ann. d. Physik **4**, 500 (1931).

stead of emission measurements of 2537 is that an exposure of 4047 could be obtained in a few minutes while one of 2537 necessitated an hour. As it is desirable to have at least ten exposures on a plate, preferably twenty or more, it is very difficult to keep conditions constant for so long a time.

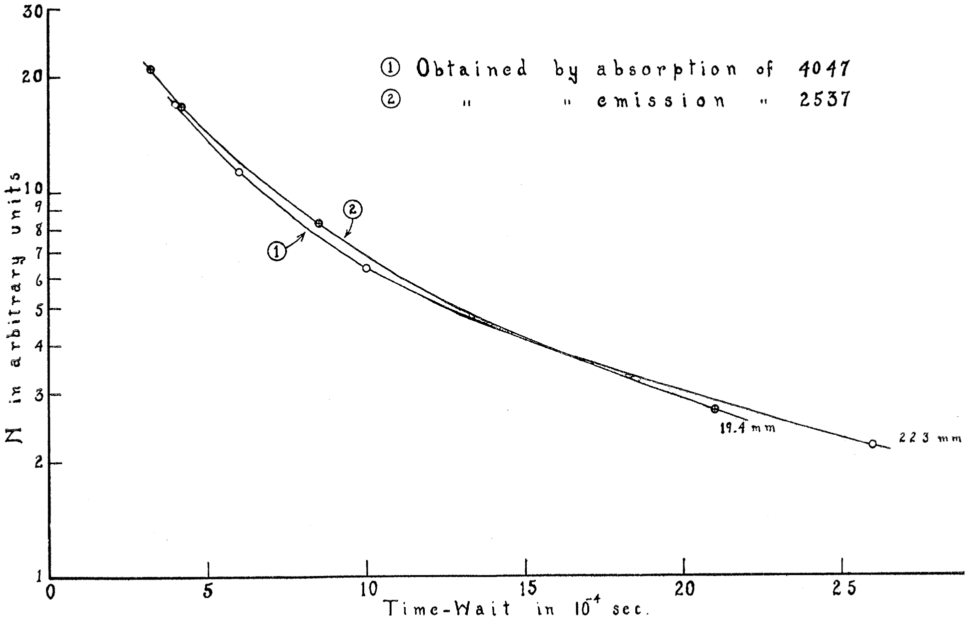

Fig. 4. Semi-logarithmic plot of the number of metastable mercury atoms as obtained from absorption of 4047 and from emission of 2537 against time after termination of optical excitation.

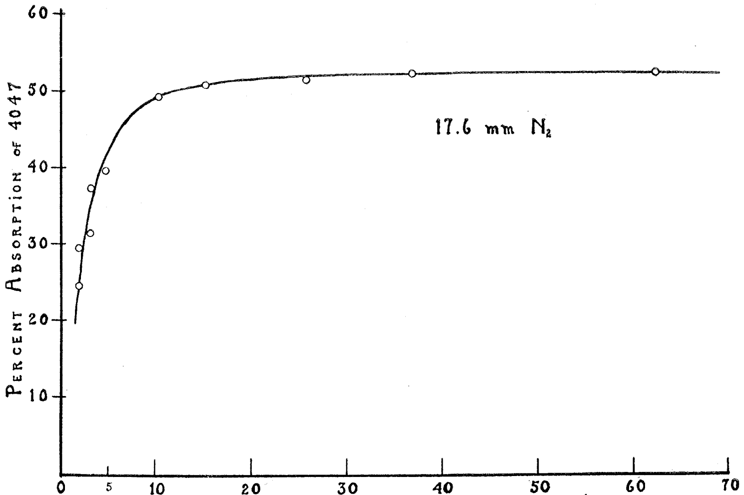

Fig. 5. Percent absorption of 4047 plotted for various time-waits after the beginning of optical excitation.

The second objection is that the concentration of Hg′, when the disk is running at high speed, might not be the same as when it is running at low speed. This point was checked by taking absorption measurements at various instants during the excitation period. Fig. 5 shows a typical curve obtained. The percent absorption is plotted against the time after the beginning of the optical excitation. The shortest excitation period used in the regular runs was 16×10^{-4} sec. It is seen from the figure that the concentration of Hg′ has practically reached a constant value by then. It may be added, parenthetically, that the life of the metastable mercury atom was also measured by a series of rate of formation curves for various pressures of nitrogen. The results are in general agreement with those obtained from the rate of decay curves, although not as accurate.

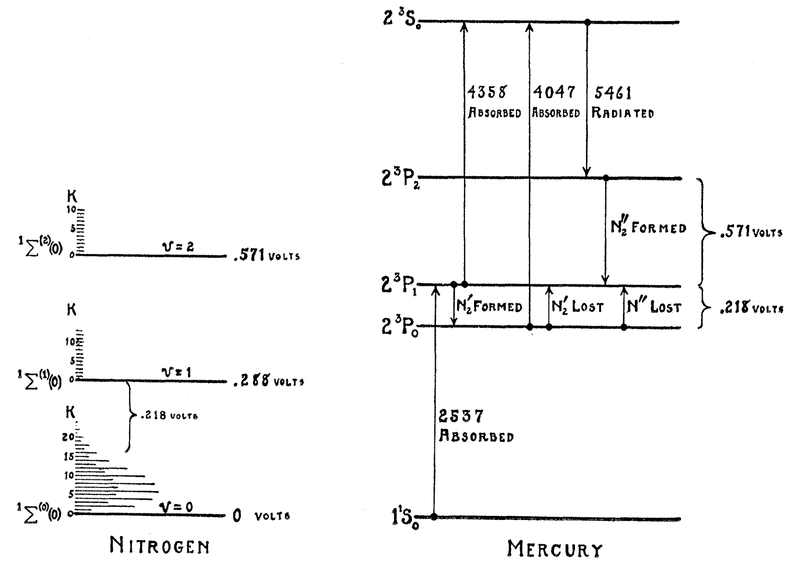

Fig. 6. Schematic diagram of a few of the energy levels of the mercury atom and of the nitrogen molecule.

DISCUSSION

It has been known for some time that nitrogen as well as a few other gases has a marked ability in producing a high concentration of 2^3P_0 states in optically excited mercury vapor. This ability seems to be connected with the energy difference between the 2^3P_1 and 2^3P_0 states of mercury and the possible vibrational energies of the molecule.[15] In the case of nitrogen the first excited vibrational state has an energy of 0.288 volts, and the second an energy of 0.571 volts. The energy difference between the 2^3P_1 and 2^3P_0 states of mercury is 0.218 volts and between the 2^3P_2 and 2^3P_1 states 0.571 volts. Fig. 6 is a schematic drawing of a few of the energy levels in mercury and nitrogen. Several of the rotation levels for nitrogen are plotted above each of the first three vibrational levels. At 20°C a greater percent of the nitrogen mole-

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[15] M. W. Zemansky, Phys. Rev. **36**, 919 (1930).

cules (11.2 percent, in fact) are in the sixth rotational state ($K=6$) than any other rotational state, as is represented by the horizontal length of the level. The lengths of the adjacent levels also bring out the fact that the statistical weight of the even levels is twice that of the odd levels.

When a mercury atom is excited to the 2^3P_1 state any one of a number of things might subsequently take place, as indicated in Fig. 6. The electron might be lifted to the 2^3S_0 level by absorption of 4358 or dropped to the 2^3P_0 level by a collision of the second kind with a normal nitrogen molecule. It has been suggested by Beutler and Rabinowitsch[16] that the nitrogen takes on vibrational energy in this type of collision. It is difficult to see how this interaction takes place unless it is the nitrogen molecules in the sixteenth or higher rotational level that are put into the first excited vibrational state by the available 0.218 volts, the amount lost by the mercury. The sixteen or more units of rotation lost by the nitrogen molecule are conserved perhaps by the Hg–N_2 system. Although only a little over two percent of the molecules are in the sixteenth level, the large cross section for collisions involving resonance as pointed out by Kallman and London[17] makes these few molecules very effective. Let ${}^2\Sigma^{(1)}$ represent a nitrogen molecule in its first excited vibrational state.[18] From the 2^3S_0 level the electron might drop to the 2^3P_2 level by emission of 5461. Since this level is also metastable we might expect the electron to remain there until a collision with a normal nitrogen molecule drops the electron to the 2^3P_1 level, and leaves the nitrogen in its second excited vibrational level, ${}^1\Sigma^{(2)}$. This is, within a few frequency units, a case of exact resonance and would be expected to take place very readily. From the 2^3P_0 level the electron might be lifted to the 2^3P_1 level by absorption of 0.218 volts from the vibrational energy of either a ${}^1\Sigma^{(1)}$ or ${}^1\Sigma^{(2)}$ molecule during the impact of a metastable mercury atom with an excited nitrogen molecule.

In the fact that there exists nearly exact resonance in the energy difference between the ${}^1\Sigma^{(2)}(k)$ and ${}^1\Sigma^{(1)}(k)$ states of nitrogen and the energy difference between the 2^3P_2 and 2^3P_1 states of mercury, probably lies the reason that no evidence for a long life 2^3P_2 metastable state has been found—even though the emission of 5461 during optical excitation is exceptionally strong.

The usual removal of the electron from the 2^3P_0 state by collisions of the first kind, diffusion to the walls, and natural decay has not been represented in Fig. 6. We see that in addition to diffusion and dissipation impacts with unexcited nitrogen, the rate of decay of the number of metastable mercury atoms may be accelerated by dissipative impacts with these excited nitrogen molecules whose number and influence also decrease with time by diffusion and by dissipative impacts.

With these ideas in mind let us consider a long cylindrical tube of radius $r=a$ filled with both normal and excited nitrogen molecules and mercury atoms. Let N'_2 be the number of nitrogen molecules per cc in the ${}^1\Sigma^{(1)}(k)$ and

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[16] H. Beutler and E. Rabinowitsch, Zeits. f. physik. Chem. **B8**, 403 (1930).

[17] H. Kallman and F. London, Zeits. f. physik. Chem. **B2**, 207 (1929).

[18] Prof. R. T. Birge suggested to me the symbol ${}^1\Sigma^{(v)}(K)$ to represent a molecule in the ${}^1\Sigma$ state with v units of vibration and K units of rotation.

$^1\Sigma^{(2)}(k)$ states; D is the diffusion coefficient of a metastable mercury atom, and D_2 is that of an excited nitrogen molecule; C is the number of collisions per sec. experienced by Hg' with N_2 that are effective in removing the mercury atom from the metastable state; C_2 is the number of collisions per sec. per excited nitrogen that are effective in removing the nitrogen molecule from excited state. E is the number of collisions per sec experienced by Hg' with excited nitrogen that are effective in removing mercury atom from metastable state. One then obtains the relations

$$\frac{\partial N}{\partial t} = D\left(\frac{\partial^2 N}{\partial r^2} - \frac{1}{r}\frac{\partial N}{\partial r}\right) - CN - ENN_2'$$

$$\frac{\partial N_2'}{dt} = D_2\left(\frac{\partial^2 N_2'}{\partial r^2} - \frac{1}{r}\frac{\partial N_2'}{\partial r}\right) - C_2 N_2'$$

We shall assume that $N = N_0 =$ constant when $t = 0$ and $r = a$; also $N = N'_2 = 0$ for $r = a$ at all time. We may separate the variables in the above equations by putting $N = TR$ and $N'_2 = T_2 R_2$ where T and T_2 are functions of the time only, and R and R_2 are functions of the radius only. One then derives

$$\frac{1}{R}\left(\frac{\partial^2 R}{\partial r^2} - \frac{1}{r}\frac{\partial R}{\partial r}\right) = -q^2$$

$$\frac{1}{T_2}\frac{\partial T_2}{\partial t} + C_2 = -q^2 D_2$$

$$\frac{1}{T}\frac{\partial T}{\partial t} + C + Ee^{-\beta t} = -q^2 D$$

where $q =$ constant and $\beta = C_2 + q^2 D_2$

The solution $J_0(qr) = R$, of the first equation together with the help of the boundary conditions fixes $q = \mu_\nu / a$ where μ_ν is one of the infinite sequence of roots of $J_0(\mu) = 0$. The final solution to a high degree of approximation is arrived at in the form

$$N = N_0 \exp\left[-\alpha t + A(e^{-\beta t} - 1)\right] \qquad (1)$$

where $\alpha = C + q^2 D$ and $A = E/\beta$.

By choosing four values of N from any one curve in Fig. 3, it is possible to solve the above expression for the unknown coefficients, α, β and A. The values of α and β are plotted in Figs. 7 and 8 against the nitrogen pressure. In Fig. 7 it is seen that the minimum value of α occurs in the neighborhood of 6 mm admixed nitrogen. For pressures less than 6 mm α increases due to increase in number of collisions of the first kind. In Fig. 8 the minimum for β is shifted to 20 mm nitrogen pressure. A shift to a higher pressure for the minimum of the coefficient for nitrogen might be expected since nitrogen diffuses more rapidly than mercury. The broken line shows an extrapolation of the curves for α and β may reasonably be made to pass through the origin. In other words the data of this experiment are not sufficiently accurate or the extrapolation is too far to indicate a value of α or β different from zero. The interpretation would be that the metastable mercury and nitrogen, contained in an infinitely large resonance cell, would have an infinite life at zero nitrogen pressure. This life may be called the natural life.

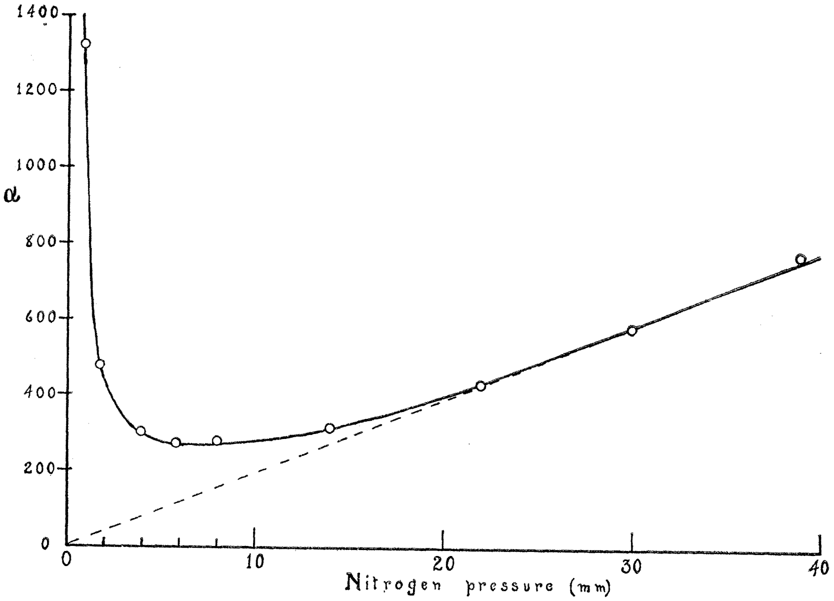

Fig. 7. Decay coefficient, α, for metastable mercury when not influenced by metastable nitrogen plotted against various nitrogen pressures.

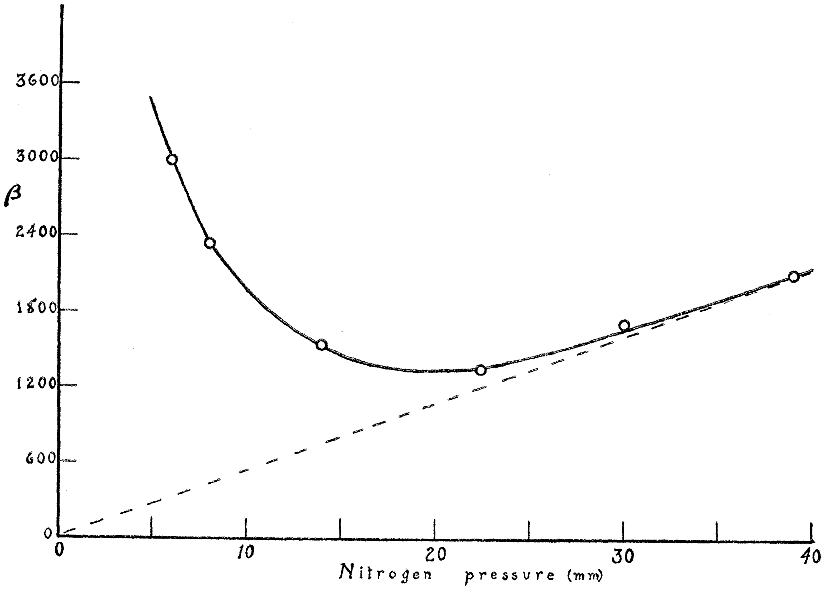

Fig. 8. Decay coefficient, β, for metastable vibrating nitrogen molecule plotted against various nitrogen pressures.

With the help of the kinetic theory of gases, it is possible by taking the values of α or β at any two pressures in Figs. 7 or 8 to calculate C and D or C_2 and D_2 respectively. From the kinetic theory we may write

$$C = 5.24\gamma\sigma^2 p \times 10^5 \qquad D = 1755/\sigma^2 p$$

$$C_2 = 6.95\gamma_2\sigma_2{}^2 p \times 10^5 \qquad D = 2320/\sigma_2{}^2 p$$

where γ is the probability that an impact involving Hg′ be a dissipative one for the Hg′, γ_2 is the probability that an impact involving Hg′ be a dissipative one for the N_2', σ and σ_2 are distances, expressed in angstroms, between centers at impact for Hg′ and N_2' respectively, p is the nitrogen pressure expressed in mm of mercury. A summary of the various values calculated from the curves of Figs. 7 and 8 are given in Table I.

Table I.

	For Hg′	For H_2'
Prob. that impact be a dissipative one	3.3×10^{-6}	$80.\times10^{-6}$
Distance between centers at impact	3.2×10^{-8} cm	0.85×10^{-8} cm
Diffusion coefficient	0.129 gm · cm^{-2} · sec.^{-1} · dyne^{-1}	2.41 gm · cm^{-2} · sec.^{-1} · dyne^{-1}
Maximum observed life	2.54×10^{-3} sec.	0.52×10^{-3} sec.
Pressure of N_2 for maximum life	6 mm	20 mm
Natural life	∞	∞

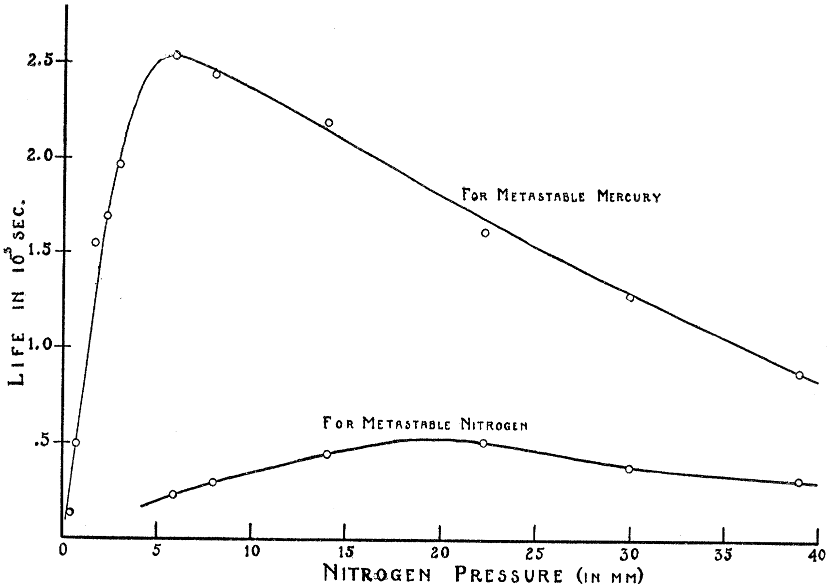

Fig. 9. Life in 10^{-3} sec. for the metastable mercury atom and vibrating nitrogen molecule as a function of various nitrogen pressures.

It must be added that the values quoted for N_2' are less accurate than those for Hg′, due perhaps to N_2' (meaning nitrogen in either its first or second excited vibrational state) functions as a second order effect.

The reciprocal of α multiplied $\log_e 2$ gives the half-value time or life of the metastable mercury atom when not influenced by vibrating metastable nitrogen molecules. Likewise $(1/\beta)\log_e 2$ gives the life of the metastable nitrogen. Fig. 9 shows a plot of these life times for various pressures of nitrogen. The life of Hg′ increases nearly linearly with small pressures of nitrogen, since the diffusion varies inversely as the pressure. For high pressures the life decreases nearly linearly with pressure, since the number of collisions of the first kind increases directly as the pressure. The maximum life for Hg′ and N_2' is seen to occur for a nitrogen pressure near 6 mm and 20 mm respectively.

If one assumes the distance between the centers for impacts involving Hg′ to be the distance between Hg′ and N_2 and the radius of N_2 is the kinetic theory radius from viscosity, then one obtains the ratio of the radii for Hg′ to Hg to be 0.89 which seems quite reasonable. For the case of N'_2 the distance between the centers at impact is given to be less than the diameter of the normal nitrogen molecule. This is, however, in accord with the recent calculations made by Zener. He calculates, for the simple case of a nitrogen molecule in its first excited vibrational state transferring its energy to a normal nitrogen molecule at room temperature, a cross section for the transfer of $0.0^{4}4\times$kinetic theory cross section; and with increase in mass of the two molecules an increase also in the resonance cross section. It must be remembered that in this experiment with mercury and nitrogen, the excited nitrogen molecule may collide with Hg, Hg′, N_2 or N_2'.

The two main points to be made in this paper are that with careful calibration of photographic plates the decay of the metastable 2^3P_0 state of mercury is found not to be accurately exponential, and that the departure from the exponential can be reasonably attributed to long-lived excited vibrating metastable nitrogen molecules.