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ON LIFE AND CONCENTRATION OF METASTABLE ATOMS AND THE QUENCHING OF MERCURY RESONANCE RADIATION

By E. Gaviola
Department of Terrestrial Magnetism, Carnegie Institution of Washington

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Abstract

A complete and general study of the dependence of life and concentration of metastable mercury atoms, optically excited, on experimental conditions, on foreign gas-pressures, and on intensity of illumination is given. This study explains why the life can not be larger than 10^{-2} second under laboratory conditions and why foreign gases act so differently in regard to the accumulation of excited atoms. The theoretical results are in good agreement with all experimental data available. An improved and more general formula for the quenching of mercury resonance radiation is obtained. The efficiencies of collisions of the second kind of metastable mercury atoms with N_2, A, and He molecules are calculated numerically. It is shown that the concentration of metastable atoms increases only with the square root of the intensity of the exciting light and not with the exciting light itself as generally assumed.

I. Life of Metastable Atoms

In a previous publication[1] I have mentioned that a provisional measurement of the transition probability of the "forbidden" line 2656 ($2^3P_0 \rightarrow 1^1S_0$) indicates that the life of a metastable mercury atoms is, when undisturbed, of the order of magnitude of 10 seconds. On the other hand all the measurements of that life made under laboratory conditions give values for it that range from 10^{-3} to 10^{-2} second. The gap between the two values is considerable. It is therefore of interest to analyze the factors that in the laboratory shorten the life so many times and to see how these factors work depending on experimental conditions. The metastable atoms that we shall consider are the ones on the level 2^3P_0. They are the only ones of importance for photosensitized fluorescence and chemical reactions. Metastable atoms are produced mainly and practically exclusively in all the cases we are considering by collisions of the second kind of resonance atoms (2^3P_1) with other molecules (Fig. 1). They are destroyed in many different ways which we shall consider one by one. Let us begin by considering a vessel with a quartz window containing saturated mercury vapor at room temperature and illuminated with the

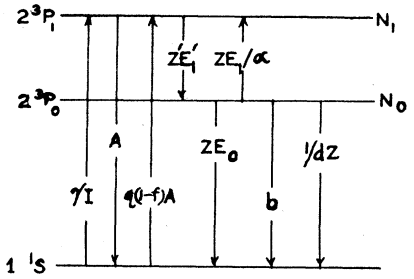

Fig. 1. Diagram of transitions regarding metastable atoms.

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[1] E. Gaviola, Phil. Mag. 6, 1181 (1928).

light of a water-cooled, magnetically-deflected, mercury arc. The intensity of illumination should not be too strong. The case of strong illumination will be considered further on. Under these conditions the few metastable atoms that will be produced will almost with certainty reach the wall owing to the long mean free path at 10^{-3} mm pressure and they will be destroyed as a result of it. All experimental evidence favors the assumption that collisions with solid walls destroy all excited atoms including metastable ones. Now owing to the fact that the resonance line is reduced to one-half 5 mm vapor, the mean distance of a metastable atom from the entrance wall when it is produced is 5 mm and since the mean thermal velocity is 1.7×10^4 cm/sec, the mean time that atoms will take for hitting the entrance wall will be of the order of a small multiple of 10^{-5} second. The presence of the other walls of the vessel will decrease that time. The mean life of a metastable atom "in vacuum" can therefore not be longer than say $1/2\times10^{-4}$ second. This time could be increased only by lowering the temperature and at the same time increasing the dimensions of the vessel. The latter alone would not help owing to the fact that at room temperature most metastable atoms will, be produced only a few millimeters away from the entrance wall and they will have a good chance of hitting this wall independent of the distance of the others. Now let us assume that we introduce slowly into the vessel a foreign gas which does not or nearly does not destroy metastable atoms by collisions of the second kind. As such we may use H_2O, N_2, A, or He, which have been freed from hydrogen. The life, τ_0, of the metastable atoms will now increase in proportion to the foreign gas pressure owing to the diminishing of the diffusion rate towards the walls. At the same time the number of collisions of a metastable atom with foreign gas molecules will increase in proportion to the pressure. Now Foote[2] has called attention to the fact that at room temperature out of 6000 molecules one has a speed sufficient to perform a collision of the first kind bringing the metastable atom to the resonance level. A metastable atom will survive then on the average only $6000/E_1$ collisions, if E_1 is the efficiency factor for collisions of the first kind. The life, τ_0, will then reach a maximum value when on the average a metastable atom suffers $6000/E_1$ collisions before hitting the walls. The maximum will be reached at a pressure of a few millimeters depending on the factor E_1. If we increase the foreign gas pressure, τ_0 will be still mainly determined by the time of $6000/E_1$ collisions, but since this time decreases with the pressure, τ_0 will decrease in proportion to the inverse pressure. Let us put all this in better form: The probability of hitting the wall is $1/(c+Zd)$, if c is the probability at pressure zero, d a constant inversely proportional to the diffusion coefficient and Z the number of gas kinetic collisions, which is proportional to the pressure. If collisions with the wall were the only death reason, the life, which we will call τ_1, would be the inverse of the probability given above

$$\tau_1=c+dZ. \tag{1}$$

This is a straight line which cuts the ordinate axis at the point c and has a slope d that depends on the diffusion constant of the particular gas and especi-

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[2] P. D. Foote, Phys. Rev. **30**, 288 (1927).

ally on the position of the volume element that we are considering in regard to the walls; for a volume element near a wall, d will have a smaller value than for an element farther away from it.

On the other hand the probability of suffering a collision of the first kind is ZE_1/α. Here α is the average number of collisions required for one of them to have sufficient energy to perform a collision of the first kind. This number is given by Boltzmann's formula $\alpha = e^{-w/kT}$ where w is the difference of energy between the 2^3P_1 and 2^3P_0 states. The life, considering only collisions of the first kind, is then

$$\tau_2 = \alpha/ZE_1. \tag{2}$$

The resultant life τ_0 is, if we take both processes into consideration, the inverse of the sum of both probabilities

$$1/\tau_0 = 1/\tau_1 + 1/\tau_2.$$

To simplify the formulas we will neglect c in (1) because it is small in comparison with dZ for all pressures above a tenth of a millimeter. We write then

$$\tau_1 = dZ \tag{3}$$

and obtain with it

$$\tau_0 = 1/(ZE_1/\alpha + 1/dZ). \tag{4}$$

Figure 2 illustrates τ_1, τ_2 and τ_0 as functions of the pressure Z assuming arbitrary values for d and E_1. We see that τ_0 is mainly limited by wall collisions at pressures below one millimeter, while it is determined mostly by collisions of the first kind beyond 4 millimeters pressure. τ_0 can be increased only by lowering the temperature (increase of α) or by choosing a gas with small

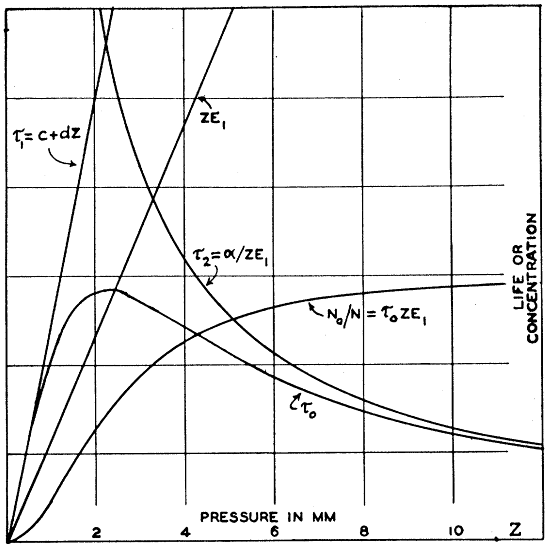

Fig. 2. Dependence of life and concentration on foreign gas pressure.

efficiency E_1. Differentiating τ_0 in regard to Z we find that τ_0 has a maximum for $ZE_1/\alpha = 1/dZ$, that is, when the probabilities of hitting the wall and suffering a collision of the first kind are equal. Now, what are the numerical values of E_1 and d for the gases that come into consideration? Under the assumptions made so far, metastable atoms are destroyed at higher gas pressures only by collisions of the first kind. Under stationary conditions the number of transitions producing metastable atoms $N_1Z'E_1'$ (Fig. 1) must be equal to the number of transitions destroying those which are N_0ZE_1/α. We have then

$$N_0ZE_1/\alpha = N_1Z'E_1'$$

and since for higher pressures $N_0 = \alpha N_1$ as we shall see presently,

$$ZE_1 = Z'E_1'. \tag{5}$$

If we set arbitrarily $Z = Z'$, which amounts to saying that the collision section of the metastable atoms shall be set equal to that of resonance atoms in every case then we see that the efficiency of collisions of the first kind, of metastable atoms, is equal to the efficiency of collisions of the second kind, of resonance atoms. These last efficiencies have been calculated in a preceding paper[3] to which we shall refer in the following, and we shall use the values given in Table II there.

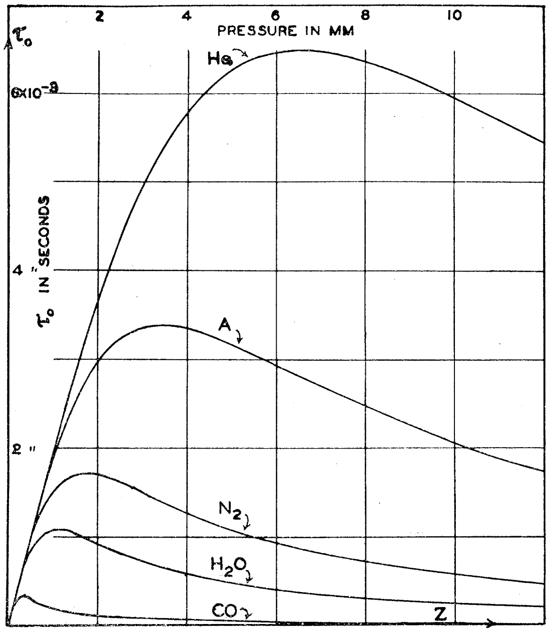

Fig. 3. Life, τ_0, as a function of the foreign gas pressure under ideal conditions.

The value of d depends primarily, as we said before, on the position of the volume element considered in regard to the walls and on the diffusion con-

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[3] E. Gaviola, Phys. Rev. **33**, 309 (1929).

stant for metastable atoms in each particular gas. This last is not known. The dependence of d on position can be calculated exactly, but we shall not do it here to avoid lengthening the paper unnecessarily. We shall assume arbitrarily $d=2\times 10^{-3}P/Z$ sec/mm (P is the pressure in millimeters) in the following for all gases. This value is in accordance with previous calculations of similar cases[4] and represents more or less an average for the experimental conditions primarily considered here. Using these numerical values we obtain the curves of Fig. 3 for τ_0. The ordinates give the life in seconds and the abscissae the pressure in millimeters.

The influence of collisions of the second kind and of impurities. So far we have assumed that collisions of the second kind of metastable atoms with foreign gas molecules have an efficiency zero. Now if an impurity in the form of H_2 or O_2 is present in the foreign gas, which will generally be the case if no special precautions are taken, this efficiency can not be zero. Moreover experimental evidence seems to show that some gases like CO have an efficiency of their own in destroying metastable atoms independent of impurities. Let us consider now how τ_0 is affected by collisions of the second kind of metastable atoms. τ_0 will be limited not only by the probabilities of hitting the wall and collisions of the first kind but also by the probability of a collision of the second kind ZE_0 if E_0 is the efficiency factor for this last type of collisions. Thus

$$\frac{1}{\tau_0}=\frac{1}{dZ}+\frac{ZE_1}{\alpha}+ZE_0=\frac{1}{dZ}+Z\left(\frac{E_1}{\alpha}+E_0\right)$$

and if we make

$$E_1/\alpha+E_0=E \tag{6}$$

then E is the total efficiency of a collision in destroying a metastable atom. τ_0 now takes the form

$$\tau_0=1/(ZE+1/dZ). \tag{7}$$

This expression is the same formula (4) of the previous case with the only difference that instead of E_1/α we have now E, which is in general slightly larger. The curves of Figure 2 then will still represent the form in which τ_0 varies with pressure, the ordinate will have to be reduced in general, and for higher pressures the reduction factor will be $E_1/\alpha E$. To give a numerical example, if we use N_2 with so much impurity in it that $E\approx 2E_1/\alpha$ then the curve that will represent N_2 in this case is the one that corresponded to water in Figure 3. (This is because E_1 water $=2E_1$ nitrogen.)

The influence of formation of molecules, absorption of light, and impurities of the vessel. It is known that in the case of a collision of a metastable mercury atom with a normal one there is a certain probability for the formation of a Hg_2 molecule. This probability will not depend on the pressure of the foreign gas. The same is true for the probabilities of absorbing lines of the arc like 4046 and of colliding with some impurity (H_2) which develops in the ves-

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[4] Meissner and Graffunder, Ann. d. Physik **84**, 1041 (1927).

sel as a result of the illumination. To these we can add the probability of emission of 2656. We will denote by b the sum of the probabilities of all these processes which do not depend on the pressure. Then

$$\tau_0 = 1/(ZE + 1/dZ + b) \tag{8}$$

is the most general expression for the life of metastable atoms.

The term b will be small in comparison with $1/dZ$ for small pressures and it will be negligible in comparison with ZE for large Z; only for intermediate pressures will it affect the curve τ_0 in which case the effect will be to flatten down the maxima of the curves of Figure 2. Altogether then we see that the form of the τ_0 curves is mainly determined by diffusion on one side and by collisions of the first and second kind on the other, and that the value of τ_0 can not under laboratory conditions be increased practically beyond say 10^{-2} second at room temperature.

II. Relative Number of Metastable Atoms

The number of metastable atoms will be under all conditions given simply by the number of such atoms produced per second multiplied by their life τ_0. Metastable atoms are produced in all cases considered here mainly and practically exclusively by collisions of the second kind of resonance atoms with foreign gas molecules. The number of atoms brought to the 2^3P_0 level per second is therefore N_1ZE_1 [Figure 1 and Eq. (5)] and the number of metastable atoms

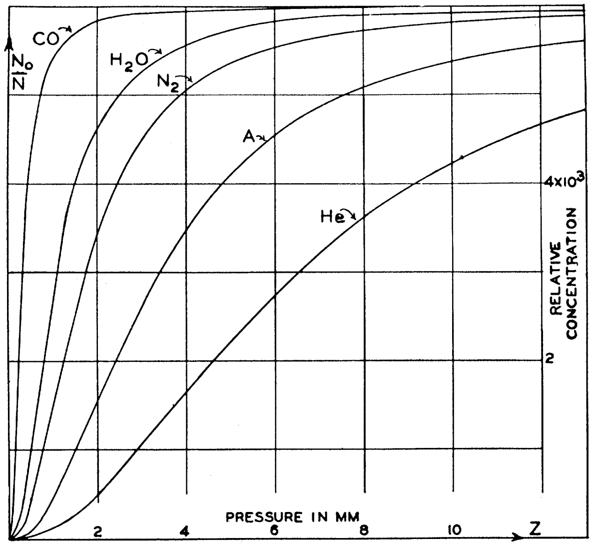

Fig. 4. Relative concentration of metastable atoms as a function of the foreign gas pressure under ideal conditions.

$$N_0 = N_1 Z E_1 \tau_0. \tag{9}$$

The ratio N_0/N_1 has been plotted in Figure 2 as a function of the pressure. We see that this ratio will increase at first with the square of the pressure owing to the fact that both ZE_1 and τ_0 increase with pressure and that it will rapidly approach the asymptotic value α. As we see, the form of the N_0/N_1 curve is very different from the one of the τ_0 curve and the maximum in the life will in general not correspond to a maximum in the concentration.

Let us now calculate N_0 under the ideal assumptions $E_0=0$ and $b=0$. τ_0 is then given by formula (4) and

$$\frac{N_0}{N_1}=\left(\frac{1}{\alpha}+\frac{1}{dE_1Z^2}\right)^{-1} \tag{10}$$

In Figure 4 I have plotted this ratio for the gases we are considering as a function of the pressure using for α, d, and E_1 the same values as before. We see that all the curves tend more or less rapidly towards the asymptotic value α given by Boltzmann's formula. A comparison of Figures 3 and 4 shows the curious result that for a given pressure the gas that allows the metastable atoms to live longest is the one which produces the smallest concentration of them. This shows again that life and amount by no means behave similarly.*

CASE $E_0 \neq 0$

If we assume that $E_0\neq 0$ the life τ_0 is given by formula (7) and the amount N_0 will be

$$\frac{N_0}{N_1}=ZE_1\tau_0=\left(\frac{E}{E_1}+\frac{1}{dE_1Z^2}\right)^{-1}$$

and if we put

$$E_1/E=\alpha' \tag{11}$$

we have

$$\frac{N_0}{N_1}=\left(\frac{1}{\alpha'}+\frac{1}{dE_1Z^2}\right)^{-1}. \tag{12}$$

This formula is identical with formula (10) with the only difference that instead of α we have now α' which is somewhat smaller than α. Formula (12) will be represented then by curves similar to the ones in Figure 4 that will converge asymptotically towards a constant value α'. This yields the interesting result that the Boltzmann distribution between 2^3P_0 and 2^3P_1 will not hold now any more even at high pressures in spite of the rapid interchange between the two levels.

The fact that N_0/N_1 becomes constant for high pressure does not mean that N_0 itself will be constant. It was so in the ideal case considered before

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* Formula (10) and the curves of Figure 4 are not exact for any particular volume element v. They are exact for the average taken over the whole volume. This is due to the fact that the metastable atoms generated in a volume element v, and which have an average life τ_0, do not stay in v owing to diffusion; they distribute more or less all over the vessel, depending on the pressure. At higher pressures when the influence of diffusion disappears, formula (10) and curves of Figure 3 will be exact also for a particular volume element. An exact calculation of the dependence of N_0 on pressure and position can be made as will be shown later.

when it was assumed that $E=0$. This however, leads to $N_1=$ constant and N_1 will no longer be constant in the case $E_0=0$.

CASE $b \neq 0$

Let us consider the influence of formation of molecules, absorption of light, and of impurities of the vessel on the amount N_0. The life τ_0 is given now by formula (8). Therefore

$$\frac{N_0}{N_1}=ZE_1\tau_0=\left(\frac{1}{\alpha'}+\frac{1}{dE_1Z^2}+\frac{b}{ZE_1}\right)^{-1} \tag{13}$$

The term b/ZE_1 will be small compared with $1/dE_1Z^2$ for small pressures and it will be negligible in comparison with $1/\alpha'$ for high pressures. The curves of Figure 4 will then represent (13) adequately for small and for large pressures (replacing α by α') but for the intermediate range the presence of b/ZE_1 will flatten down the curves.

To obtain N_0 itself as a function of the pressure we have to multiply (13) by N_1. The values of $N_1=f(Z)$ can be obtained from the quenching curves of Stuart[5] or they can be calculated directly. We shall do the latter because with the help of Stuart's curves we shall be able to obtain the numerical values of E_0 and of b for some of the gases.

III. THE QUENCHING OF RESONANCE RADIATION

The quenching of mercury resonance radiation originally calculated by Foote in a very interesting paper[2] has been recently treated by Klumb and Pringsheim[6] in a more complete and very elegant way. The latter authors restricted themselves to the calculation of N_0 and did not take into consideration the reabsorption factor $q(1-f)$. To avoid repetition, I have used here Klumb and Pringsheim's results in the calculation of N_1 paying attention to the factor $q(1-f)$, and without neglecting the term τ/T_c^0 (in Klumb and Pringsheim's symbols). I give here therefore the expression for N_1 and refer to the publication[6] for its deduction. It is

$$\left(1-\frac{q}{2}\right)\frac{N_1}{N_1^0}=\left\{1+\frac{(ZE_0+b)\tau/(1-q/2)}{1/\alpha'+1/dE_1Z^2+b/ZE_1}\right\}^{-1}=J \tag{14}$$

where $N_1^0/(1-q/2)$ is the number of resonance atoms for $Z=0$, τ their mean life at $Z=0$, and q the reabsorption factor. $(1-q/2)N_1/N_1^0=J$ is proportional to the amount of resonance radiation observed and it represents the value directly measured by Stuart. For pressures above a few millimeters diffusion can in general be neglected and therefore we can put $1/dE_1Z^2=0$. Then (14) goes over into

$$J=\left\{1+\frac{(ZE_0+b)\tau/(1-q/2)}{1/\alpha'+b/ZE_1}\right\}^{-1} \tag{15}$$

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[5] H. Stuart, Zeits. f. Physik **32**, 262 (1925).

[6] H. Klumb and Peter Pringsheim, Zeits. f. Physik **52**, 610 (1928).

Formula (15) is identical with formula (10) of Foote[2] if we translate his constants in the following way: $p \rightarrow Z$, $c \rightarrow b$, $b \rightarrow E_1$, $d \rightarrow E_1/\alpha$, $e \rightarrow E_0$ and $fr \rightarrow (1-q/2)/\tau$. We can therefore rectify (15) in the same way in which Foote did with his formula. We can thus write it as follows:

$$\frac{\alpha\tau/(1-q/2)}{1/J-1}-\frac{\alpha}{ZE_1}=\frac{1}{ZE_0+b} \qquad (16)$$

If we plot therefore the inverse of the quantity at the left using Stuart's values for J, we will obtain for pressures above a few millimeters a straight line, the slope of which will give us E_0, and its value for $Z=0$ will be equal to b. Table I gives the values used and the results obtained in that way. We have set $q=1/4$ as in the paper referred to in footnote 3.

TABLE I

Gas	Z	ZE_1	E_1	b	ZE_0	E_0
CO	$28. \times 10^6 p$	$28. \times 10^6 p$	1	—	—	—
H_2O	6.4 "	2.5 "	0.4	—	—	—
N_2	6 "	1 "	0.2	1300	87	$15. \times 10^{-6}$
A	5 "	0.26 "	0.05	570	10	2 "
He	14 "	0.071 "	0.005	330	3	0.2 "

The values of b and E_0 for CO and H_2O cannot be obtained in this way due to the neglect of diffusion. We have seen that our calculation is correct only for pressures above a few millimeters; the quenching curves of CO and H_2O are only known for a few millimeters pressure and therefore an estimation of b and of E_0 cannot be made in this way for these gases. The values of b and E_0 obtained for N_2, A, and He are probably correct and give an idea of the experimental conditions of Stuart. We cannot ascribe to these values any specific meaning because b is the sum of the probabilities of four independent processes: emission of 2656, formation of molecules, absorption of light, and collisions with vessel impurities; and E_0 embodies collisions of the second kind with foreign gas molecules and with impurities that may be present. If we arbitrarily interpret E_0 as solely due to impurities (H_2) we would have to assume that Stuart had one molecule of hydrogen in 10,600 of N_2, in 66,500 of A, and in 1,860,000 of He. These values differ greatly from the ones obtained by Foote assuming $E_1=1$ for all processes (see his Table II), and are more likely to correspond to experimental conditions.

IV. ABSOLUTE NUMBER OF METASTABLE ATOMS

Now that we have obtained the expression for N_1 and the numerical values of E_0 and b we can return to our metastable atoms. Multiplying (14) and (13) we obtain

$$N_0=N_1^0/(1-q/2)/\left[1/\alpha'+(ZE_0+b)\tau/(1-q/2)+1/dE_1Z^2+b/ZE_1\right] \qquad (17)$$

as the final expression for the amount of metastable atoms as a function of the pressure. We know now all the constants entering in (17) and we can therefore plot N_0 as a function of the pressure Z. This has been done in Figures

5 and 6 for the gases we are considering. We would obtain the same curves for N_2, A, He, using formula (13) and for N_1 the values taken from Stuart's curves. The ordinates of Figures 5 and 6 indicate the number of metastable atoms in a volume unit assuming that $N_1^0 = 1$; that is the unit of volume absorbs 10^7 light quanta of 2537 per second. As long as the illumination is not too strong the values of N_0 for each pressure will be directly proportional to the absorbed light intensity. We shall consider presently the case of strong illumination. As said before we could not obtain the values of b and E_0 for CO and for H_2O owing to the neglect of diffusion. The curves for these two gases in Figures 5 and 6 have been obtained using formula (17) and assuming arbitrarily $b = 1300$, $E_0 = 14 \times 10^{-6}$ for H_2O and $b = 1300$, $E_0 = 177 \times 10^{-6}$ for CO. These values have been chosen so that for N_0 they give curves that are in agreement with the previous experimental results of the author.[1] They probably do not correspond to the experimental conditions of Stuart.

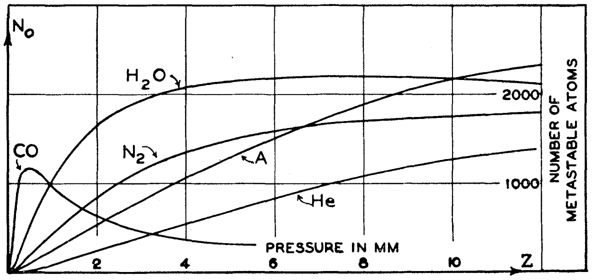

Fig. 5. Number of metastable atoms as a function of the foreign gas pressure if 10^7 quanta are absorbed per second.

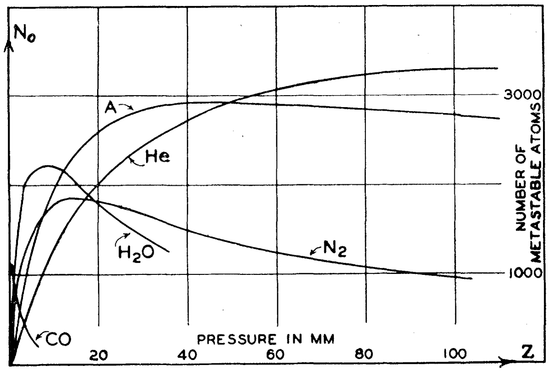

Fig. 6. Number of metastable atoms as a function of the foreign gas pressure for $N_1^0 = 1$ (10^7 quanta absorbed per second).

Let us see how the values of E_0 and b influence the shape of our curves N_0. A large E_0 (impurities proportional to the pressure) will displace the maximum of N_0 towards smaller pressure without flattening it much and at the same time it will make N_0 decrease rapidly for higher pressures; a large b (impurities independent of pressure) will displace the maximum towards higher pressures and it will flatten it considerably. This last has been experimentally shown by Klumb and Pringsheim admitting a constant small amount of H_2 together with the nitrogen[6] (Figure 4, p. 618 in Klumb and Pringsheim's paper). The curves of Figures 5 and 6 are in general qualitative and sometimes even quantitative agreement with the experimental results of Donat,[7] Loria,[8] Klumb and Pringsheim,[6] Pool,[9] and Gaviola.[1] So for instance, the curves for the intensity of the photo-sensitized fluorescence of thallium as a function of the pressure of argon obtained by Donat are in very good agreement with the A curve of Figure 6; he found maxima for all the lines at 40-mm pressure and we see that this corresponds exactly to the maximum in the amount of metastable atoms. Since according to Loria at low pressure, N_2 is more efficient than A and according to Donat the reverse is true at high pressures, we see that the apparent contradiction between their results is removed and conciliated by Figure 5. The fact that Klumb and Pringsheim obtain a maximum in the nitrogen curve already at 1 mm pressure, would indicate that they measured the absorption of 4047 at some distance from any wall so that their diffusion curve (τ_1 in Figure 1) was very steep, which corresponds to a large d. The result obtained by Klumb and Pringsheim with water is almost certainly due to the pressure of free hydrogen mixed with the water vapor. According to my experience water vapor contains always some free hydrogen even before it is illuminated with the arc. Finally the curve obtained by Pool for $N_0(a)$ as a function of the nitrogen pressure is in very good agreement with our N_2 curve (Figure 6). The curve of Pool for $\tau_0(b)$ as a function of the nitrogen pressure is also in good general agreement with our curve of Figure 3. It ought to be mentioned though that according to our theory the τ_0 curve ought to increase linearly starting from zero, which the $\tau_0(b)$ curve of Pool does not do. I am not able to explain this divergence.

For a given illumination the maximal concentration of metastable atoms that can be obtained is then primarily limited by the ratio $\alpha = e^{-w/kT}$ and by the amount of impurities contained in the admixed gas. α can be increased by lowering the temperature T, but this would diminish rapidly the density of the mercury vapor in the vessel, so that no real gain would result. We can increase N_0 only by increasing the intensity of the primary light, but this has also a limit as we shall see in the following paragraph.

V. Dependence on Illumination

So far we have disregarded collisions between two excited atoms. As long as the illumination is not strong the number of excited atoms will be small in comparison with the number of normal atoms and collisions between two metastable atoms will occur rarely. But if we increase constantly the intensity of the exciting light, the number of metastable atoms will increase at first linearly with it and the probability of a collision of two metastable atoms will grow with the square of the illumination. Now Beutler and

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[7] K. Donat, Zeits. f. Physik **29,** 345 (1924).

[8] S. Loria, Phys. Rev. **26,** 573 (1925).

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

Josephy[10] have shown that by a collision of two metastable atoms there is a great probability for one of them to take over the whole energy, the other becoming normal. Both metastable atoms cease then to be such as a result of the collision. This process will put an additional limit to the life and concentration of metastable atoms.

The life was given in the general case by formula (8). It will be diminished now by the additional probability of hitting another metastable atom, which will be proportional to their number N_0. We will call it cN_0. Then

$$\tau_0 = (ZE+1/dZ+b+cN_0)^{-1} = (a+cN_0)^{-1} \tag{18}$$

if we put the part independent of the illumination

$$(ZE+1/dZ+b)^{-1} = 1/a. \tag{19}$$

On the other hand, the number N_0 is given always by formula (9)

$$N_0 = ZE_1N_1\tau_0$$

in which N_1 is proportional to the intensity of illumination I. We can write then

$$N_0 = hI\tau_0 \tag{20}$$

where h is a factor of proportionality. Combining (18) and (20) we obtain the quadratic expression

$$cN_0^2 + aN_0 - hI = 0 \tag{21}$$

and its solution is

$$2cN_0 = (a^2+4chI)^{1/2} - a. \tag{22}$$

As we see N_0 will increase only with the square root of the light intensity. We obtain in the same way for the life

$$\tau_0 = [(a^2+4chI)^{1/2} - a]/2chI. \tag{23}$$

τ_0 will then decrease at the same time as N_0 increases. Now Klumb and Pringsheim[6] have observed that the absorption of the line 4047 does not increase in proportion to the illumination I if N_2 at pressures above 0.05 mm is present. The absorption reaches a certain saturation at a value of 0.55. They explain this by pointing out that since the cold vapor absorbs only the core of the line of the arc, once the whole core is absorbed no further absorption can take place. Their explanation is surely correct. It may be but one factor in the phenomenon since formula (22) shows that we can expect N_0 to grow only with the square root of the illumination. The curves of Figure 6 in Klumb and Pringsheim's paper could very well be reproduced using formula (22) assuming a suitable value for c. A repetition of Klumb and Pringsheim's experiment using two absorption vessels of equal section and different length would show how much of the saturation in the absorption is due to the different widths of the arc and absorption lines and how much to collisions between two metastable atoms.

The considerations and formula developed here for the metastable atoms of mercury apply, *mutatis mutandis*, to any metastable molecules excited optically.

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[10] H. Beutler and B. Josephy, Phil. Mag. **5**, 222 (1928), Naturwiss. **15**, 540 (1927).