# THE EFFICIENCY OF OUENCHING COLLISIONS AND THE RADIUS OF THE EXCITED MERCURY ATOM

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#### **ABSTRACT**

The evidence in favor and against the assumption of Foote that every collision of a foreign gas molecule with an excited mercury atom is efficient in quenching the resonance radiation is discussed, and a new calculation of the efficiency of collisions is given, based on Stuart's measurements, which shows that the efficiency can be assumed to be equal to one in the case of CO,  $H_2$ , and perhaps  $O_2$ , but that it is undoubtedly smaller than one for  $H_2O$ ,  $N_2$ , A, and He. CO has actually a greater quenching efficiency than  $H_2$ . The *radius of the excited mercury atom* is calculated using an improved value for the amount of resonance-radiatidn re-absorbed in the resonance vessel and found to be  $r_{\text{Hg}'} = 2.91 \times 10^{-8}$  cm, or 1.62 times larger than the radius of the normal atom for the case of H<sub>2</sub>, and  $r_{\text{Hg}} = 5.5 \times 10^{-8}$  cm or three-fold normal for the case of CO. The apparent higher quenching efficiency of oxygen than hydrogen is explained by the partial oxidation of the mercury vapor and consequent decrease of the density of the last. It is shown that the life of metastable atoms increases with the admission of certain foreign gases into the fluorescence vessel.

### **INTRODUCTION**

HE quenching of mercury resonance radiation by foreign gases, first observed by Wood<sup>1</sup> and later studied by Cario,<sup>2</sup> was carefully measure by Stuart<sup>3</sup> in a large range of pressure using several different gases. Stuart found that gases behave in a qualitatively similar manner, in that their effectiveness in quenching the resonance radiation follows a more or less exponential function of the pressure, but that quantitatively they differ widely. Oxygen and hydrogen, for instance, decrease the resonance radiation to one-half' its original value at pressures as low as 0.<sup>2</sup> mm while with argon and helium it is necessary to approach atmospheric pressure to obtain the same result. Since the number of collisions per second of an excited Hg atom with the molecules of the foreign gases is of the same order of magnitude for all the gases, according to the kinetic theory, Stuart was forced to assume, in order to interpret his experimental results, that the efficiency of the collisions was widely different for the different gases. While every collision of an excited mercury atom with oxygen and nearly every one with hydrogen should be a collision of the second kind, only 1 in 77 would be effective with nitrogen, <sup>1</sup> in 500 with argon, and 1 in 3300 with helium. Furthermore, the number of collisions calculated on the basis of the gas theory, assuming the gas-kinetic collision section for the Hg atom, was not sufficient in the case of oxygen and of hydrogen to explain the observed decrease of2537, and Stuart made the plausible assumption that the section of the excited atom should

<sup>2</sup> G. Cario, Zeits. f. Physik 10, 185 (1922).

<sup>3</sup> H. Stuart, Zeits. f. Physik 32, 262 (1925).

<sup>&</sup>lt;sup>1</sup> R. W. Wood, Phys. Zeits. 13, 353 (1912).

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be larger than that of the normal atom. Assuming quenching efficiency of oxygen equals 1, he calculated the diameter of the excited mercury to be 3.4 times the diameter of the normal atom. The efficiencies of the other gases, given above, were determined using this section for Hg, and applying the gas-kinetic formula for the number of collisions at the pressure at which the resonance radiation is decreased to one-half its original value. In a continuation of the work of Stuart, Cario and Franck<sup>4</sup> observed that an increase of the temperature diminished apparently the quenching efficiency of  $N_2$  so that at 750 $\degree$  forty mm of nitrogen would not affect the intensity of the resonance-radiation, while the same amount at room temperature would decrease it to one-third. To explan this curious behavior they applied a hypothesis of Joffe and Franck, according to which the life of the metastable  $2^{3}P_{0}$  atoms formed by collisions of the second kind of the resonance atoms with  $N_2$  would end at higher temperatures mainly by collisions of the first kind with high-speed gas molecules, which would bring them back to the resonance level; the quenching due to collisions of the second kind bringing atoms down to the metastable level would be neutralized by collisions of the first kind which restore the atoms to the original excited level. Foote' applied the same consideration to the case of room temperature: If the non-quenching of  $N_2$  at high temperatures (quenching efficiency = 0) can be explained by collisions of the first kind of the metastable atoms, perhaps the small efficiencies observed by Stuart for rare gases can be explained in the same way. In fact, Foote calculated that at room temperature about I/6000 of the molecules have a kinetic energy suFficient to perform a collision of the first kind with a metastable atom bringing it to the resonance level and since the life of the metastable atom is known to be about or larger than 6000 times the life of the resonance atom, collisions of the first kind may account completely for the apparent low efficiencies of Stuart. Foote assumed then, that every collision of a resonance atom with any foreign gas molecule is effective and is a collision of the second kind, which brings the atom either to the normal level (case of  $H_2$ ) or to the metastable level  $2^{3}P_0$  (case of N<sub>2</sub>, A, He, etc.). At the metastable level the atoms accumulate, because of their long life, until they are brought up again to the resonance level by a collision of the first kind; some of the metastable atoms will die before that happens, owing to collisions of the second kind with impurities and to formation of Hg<sub>2</sub> molecules. The quenching observed by Stuart with rare gases is then according to Foote only due to the presence of impurities (H<sub>2</sub> or  $O_2$ ) and to the formation of molecules. If we increase the temperature of the foreign gas, that is the number of high-speed molecules, the probability for a metastable Hg atom to suffer a collision of the first kind will increase exponentially while the probabilities of meeting an impurity or of forming a  $Hg<sub>2</sub>$  molecule will increase only with the square root of the temperature, so that above a certain temperature the two last processes will be negligible in comparison with the first and no quenching of the resonance radiation will

<sup>4</sup> G. Cario u. J. Franck, Zeits. f. Physik 37, 619 (1926).

<sup>5</sup> P. D. Foote, Phys. Rev. 30, 288 (1927).

take place; the excited atoms will simply play between the resonance and the metastable levels but when they go down to the normal level they will emit the resonance line. This is what Cario and Franck observed.<sup>6</sup> From the hypothesis outlined above Foote developed a theory which was capable of reproducing the curves of Stuart by assuming the necessary amount of impurities and the necessary rate of formation of  $Hg_2$  molecules for each case.

# THE RATIO f IN FOOTE'S THEORY AND THE DIAMETER OF THE EXCITED ATOM

Stuart obtained his value 3.4 for the ratio of the radius of the excited to the normal atom by assuming 100 percent quenching efficiency for the

case of oxygen; Foote calculated this same ratio to be  $1.15$  assuming  $100$  percent efficiency for hydrogen, ignoring the apparently higher efficiency of oxygen, and introducing a factor  $f$  in his formula, which takes care of the re-absorption of part of the resonance radiation in the same resonating Fig. 1. Diagram illustrating Hg-vapor. Foote's calculation for the case of H<sub>2</sub> is Foote's calculation for H<sub>2</sub>. illustrated by the diagram reproduced here (Fig. 1).



From the  $\gamma I$  quanta of primary light absorbed,  $AN_1$  are emitted as resonance radiation and Z  $E_1N_1$  are used for collisions of the second kind if Z is the number of collisions and  $E_1$  the efficiency of them; from the  $AN_1$ quanta radiated  $fAN_1$  escape the vessel and  $(1-f)AN_1$  are re-absorbed in it.

In the stationary case therefore

$$
AN_1+ZE_1N_1=\gamma I+(1-f)AN_1
$$
 and  $N_1=\gamma I/(fA+ZE_1)$  (1)

Now,  $fAN_1$  is the observed resonance radiation and if we call J the ratio of it to the absorbed radiation  $\gamma I$ , we have

$$
J = f A N_1 / \gamma I = 1 / (1 + Z E_1 / f A)
$$
 (2)

Assuming with Foote that every collision with hydrogen is effective  $(E_1 = 1)$ we have

$$
J = 1/(1 + Z/fA). \tag{3}
$$

Now to apply this formula to Stuart's results it is necessary to make an estimation of the factor f. Foote estimates that from the resonance radiation one-half is re-absorbed in the vessel in the case of Stuart and puts  $f = 1/2$  in

<sup>6</sup> O. Oldenberg, Zeitz. f. Physik 49, 609 (1928) has found recently that the quenching due to argon *increases* about five times if we raise the temperature to 750°, while with nitrogen, as found by Cairo and Franck it decreases to zero. This behavior of argon is difficult to understand and seems to be in contradiction with other evidence. It is possibie that it may be due simply to some impurity which develops in the tube when heated. Oldenberg found namely (see footnote, p. 611, l.c.) that in some cases even  $N_2$  showed a higher quenching power at 750', but he disregarded this result because it contradicted the previous result of Cario and Franck.

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his following calculations. But he does not consider what occurs with the re-absorbed radiation. This is what we shall do. Let us consider the resonance vessel  $R$  (Fig. 2) illuminated with parallel or slightly convergent light  $I$ and observed in the direction  $J$  from a certain distance, large as regards the diameter of  $R$ . Let us suppose first that the foreign gas pressure is zero, that is, that there are practically no quenching collisions. Then the whole absorbed and re-absorbed intensity will be radiated sooner or later as spherical

$$
PUMP \longleftarrow R \qquad j
$$
\n
$$
Fig. 2.
$$

waves with centers inside  $R$  and the factor  $f$  will be equal to 1. Let us suppose, second, that we have several mm of hydrogen in  $R$ , that is, that the resonance radiation is reduced to a small fraction by collisions of the second kind, then from

the emitted resonance radiation one-half will be re-absorbed before leaving the vessel as calculated by Foote, and this half will be practically destroyed by collisions of the second kind, so that only the first half will be observed and  $f$  will be equal to one-half. The value of  $f$  depends then on the quenching coefficient  $J$  and lies between  $1/2$  and 1. The following series gives the value of  $f$  as a function of  $K$  where

$$
K = 1/(1 + Z/A) \tag{4}
$$

is the ratio of the excited atoms that emit resonance-radiation,

$$
f = 1/2 + K/4 + K^2/8 + \cdots + K^n/2^{n+1} + \cdots
$$
 (5)

We see that for  $K=1$ ,  $1/2$ ,  $0, f=1$ ,  $2/3$ ,  $1/2$ . Foote considered only the first term of the series. For the case of equal probability of emission and collision of the second kind  $(K = 1/2)$ ,  $f = 2/3$ , and for the case of reduction of the resonance radiation to  $1/2$ ,  $(J=1/2)$ ,  $f=0.705$  and  $K=0.585$ , value cal-

	0.2	O.4 O.6			0.8	
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0.6			F(K)			

culated by successive approximations.<br>The lower curve of Fig. 3 gives f as a function of K, calculated according to the function of  $K$ , calculated according to the series  $(5)$  and the upper curve represents  *as a function of*  $*J*$ *, obtained by successive* approximations using formula  $(3)$  and (4) and the previous curve.

If we calculate now the collision radius of the excited Hg atom using  $j=0.705$  in Fig. 3. Values of f as function of formula (3) given above, the known gas quenching coefficient J and of K. kinetic formula for the number Z of kinetic formula for the number  $Z$  of collisions (formula 7) and the half pressure

0.217 mm found by Stuart for H<sub>2</sub>, we obtain  $r'_{\text{Hg}} = 2.91 \times 10^{-8}$  cm, and since the radius of the normal atom is  $r_{\text{Hg}} = 1.80 \times 10^{-8}$  it is  $r' = 1.62 \times r$ . The radius  $2.91 \times 10^{-8}$  cm for the excited Hg atom is larger than the one calculated by Foote  $(2.03\times10^{-8})$  but two times smaller than the value  $5.95\times10^{-8}$  of Stuart. We shall use this newly calculated radius in the following considerations.

### THE CASE OF OXYGEN

One objection made against Foote's theory' is that he ignores the fact that oxygen seems to have a greater quenching efficiency than hydrogen. Cario in 1922, who first calculated the radius of the excited Hg atom, already suspected that the quenching efficiency of air in Wood's original experiments in 1912 may have been due in part to a partial oxidation of the mercury vapor, and for this reason he went over to the use of rare gases in quenching experiments. This suspicion has been plainly proved in the work of Wood and Gaviola<sup>8</sup> from the conditions for the appearance of the forbidden line 2656 of Hg. There they found that if the illumination of the resonance tube is sufficiently strong, the admission of a few thousandths mm of oxygen is sufficient to destroy completely all fluorescence, including the resonance radiation of 2537. The same amount of hydrogen did not produce any noticeable effect upon the resonance-radiation. Oxygen would appear to have in this case an efficiency many hundred times higher than that of hydrogen. But Gaviola and Wood found also that the absorption of the primary light disappears at the same time, showing that no atomic mercury vapor is present in the tube. The explanation of this curious phenomenon is that mercury-oxide is formed as a result of the excitation of the mercury atoms, and the velocity of this oxidation is proportional to the intensity of the illumination. If the illumination is weak as in the case of Stuart, the oxidation will be slow and the mercury vapor will be partly replaced by the evaporation of the mercury drop contained at the bottom of the tube; if the illumination is strong as in the case of Wood and Gaviola the whole Hg vapor is oxidized in a fraction of a second and the new evaporating vapor is immediately destroyed as soon as it enters the illuminated zone. The apparent quenching efficiency of oxygen depends then on the intensity of the illumination. The reaction involved is probably

 $Hg' + O_2 \rightarrow Hg + O_2'$ ;  $O_2' + O_2 \rightarrow O_3 + O$ ;  $O_3 + Hg \rightarrow O_2 + HgO$ ;  $O + Hg \rightarrow HgO$ 

Every excited Hg atom is thus capable, under favorable conditions, of producing two mercury-oxide molecules. This accounts satisfactorily for the anomalous behavior of oxygen.

## THE EFFICIENCY OF QUENCHING COLLISIONS

The assumption made by Foote is that collisions of atoms in the resonance-level with gases are always effective and that collisions of metastable atoms are either completely inefficient in the case of rare gases and  $N_2$ , or completely effective in the case of  $H_2$  and  $O_2$ , that is, if we call E the efficiency, that  $E$  can either be 1 or 0 but can not assume an intermediate value. This assumption appears too simple to be true. In fact, CO, for instance, has clearly some efficiency in destroying metastable atoms, but this efficiency is

See for instance, M. W. Zemansky, Phys. Rev. 31, 812 (1928).

<sup>8</sup> R. W. Wood and E. Gaviola, Phil. Mag. 6, 271 (1928).

<sup>&</sup>lt;sup>9</sup> E. Gaviola and R. W. Wood, Phil. Mag. 6, 1191 (1928).

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by no means as large as the efficiency of  $H_2$  or  $O_2^{10}$ , which means that E in this case has a value actually between 0 and 1. Foote himself found that for the formation of  $Hg_2$  molecules by collisions of metastable atoms with normal ones he had to admit an efficiency of about 0.07 in contradiction with his general assumption of "100 percent efficiency in all processes." Furthermore in a recent paper by Gaviola and Wood,<sup> $9$ </sup> we have seen that collisions of resonance atoms with water molecules lead in most of the cases to formation of metastable atoms but in some of them to dissociation of the  $H<sub>2</sub>O$  molecule into H and OH and still in some other cases to formation of a  $(Hg H<sub>2</sub>O$ ) complex molecule, which shows that neither of these processes can have 100 percent efficiency. Another hint making probable that the efficiency of argon is neither 0.002 as calculated by Stuart nor 1 as assumed by Foote, is given by the results of Donat;<sup>11</sup> he illuminated a mixture of Hg and Tl vapor with 2537 and measured the increase of the intensity of the Tl lines when argon was admitted to the tube. Donat found that all lines reach a maximum at an argon pressure of 40 mm. Orthmann and Pringsheim<sup>12</sup> pointed out that since the pressure at which 2537 is reduced to 1/2 by argon is 240 mm according to Stuart, it was difficult to understand why a maximum is reached so far below the half-pressure. They tried to explain it by assuming that the excited Tl atoms were strongly quenched by the admitted argon.

On the other hand, if we assume with Foote an efficiency 1 for argon collisions, we ought to expect the maximum in the intensity of Tl lines at pressures of a few millimeters, which does not take place according to Donat's results. That the efficiency of A collisions is smaller than the efficiency of  $N_2$  ones is shown by the investigation of Loria<sup>13</sup> on the photosensitized fluorescence of thallium vapor. Loria compares the increase of the thallium lines due to the admission of argon and of nitrogen and he finds that "at very low pressures  $\cdots$  the effect of  $N_2$  may be even much stronger than that of A. It is enough to introduce into the tube a small fraction of a millimeter of carefully purified  $N_2$  (about  $2 \times 10^{-3}$  mm) to make the whole window shine with vivid, very bright soft green light" (p. 579, l.c.). Now, at very low pressures (less than 1 mm) collisions of the first kind can be neglected, as we shall see presently, and therefore the amount of metastable atoms of which the intensity of the green thallium light is an indicator (metastable atoms produced by collisions of the second kind with the foreign gas) is simply proportional to the efficiency of the last collisions. The observation of Loria shows then that the efficiency of nitrogen collisions with resonance atoms is "much stronger" than that of argon collisions. But we can calculate the efficiency of quenching collisions for each foreign gas simply from the curves of Stuart.<sup>3</sup> The reason Stuart found too small efficiencies for the rare gases is that he used only the pressure at which  $J=1/2$  for calculating them. At

<sup>&</sup>lt;sup>10</sup> E. Gaviola, Theory II, Phil. Mag. 6, 1167 (1928).

<sup>»</sup> K. Donat, Zeits. f. Physik 29, 345 (1924).

<sup>&</sup>lt;sup>12</sup> W. Orthmann and P. Pringsheim, Zeits. f. Physik 35, 626 (1926).<br><sup>13</sup> S. Loria, Phys. Rev 26, 573 (1925).

such pressure collisions of the first kind with high-speed molecules bring metastable atoms back to the resonance level and compensate in part or in full the quenching action of the foreign gas. Since at room temperature 1 in 6000 molecules has a speed sufficient to bring a metastable atom up to the resonance level the necessary condition for the occurrence of the process to an appreciable extent is that the metastable atoms live at least 6000 times longer than the resonance ones, that is about  $10^{-3}$  sec. (as pointed out by Foote). Now at pressures below a few millimeters the life of the metastable atoms is shorter than this because of collisions of the second kind with the walls of the tube: for the diffusion rate towards the wall is proportional to the inverse pressure and at low pressures a large number of metastable atoms will collide with the walls before they live  $10^{-3}$  sec. Their life at  $10^{-3}$  mm pressure (saturated Hg vapor at room temperature) cannot be much longer



Fig. 4. Efficiency curves for  $H_2O$ ,  $N_2$ , A and He.



Fig. 5. Efficiency curves for A and He.

than  $3\times10^{-5}$  sec. (the mean distance from the wall is 0.5 cm and the mean velocity  $1.7\times10^{-4}$  cm/sec.). The influence of collisions of the first kind will then disappear as we lower the pressure. If we calculate then the efficiency as a function of the pressure from Stuart's measurements we should expect it to increase as the pressure diminishes and to approach a value for  $p = 0$ which is the real efficiency coefficient. From formula (2) we obtain for the efficiency

$$
E_1 = fA(1 - J)/JZ\tag{6}
$$

where  $J$  is the value measured by Stuart,  $f$  the corresponding re-absorption factor (Fig. 3), A the emission-probability of  $2537 = 1/(1.1 \times 10^{-7})$ , and Z the number of collisions per sec.

$$
Z = 2.608 \times 10^{-22} \times \sigma^2 \times p \times ((m+m_1)/m \times m_1)^{1/2}
$$
 (7)

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if  $\sigma$  is the sum of the radii of the two colliding molecules and  $\phi$  the pressure in mm. The efficiency curves for  $H_2O$ ,  $N_2$ , A and He are given in Figs. 4 and 5. We see that the efficiencies really increase as the pressure goes down which proves the assumption that the life of the metastable atom *decreases* at low pressures because of collisions with the walls of the vessel. It is very interesting that the life of metastable atoms can be lengthened by admitting a foreign gas. This effect has been expected by several investigators<sup>14</sup> but it is shown for the first time here, as a result of experiments, that it really exists. \*

Extrapolating the curves to zero pressure we obtain the following efficiencies: 0.2 for  $H_2O$ , 0.1 for  $N_2$ , 0.03 for A, and 0.003 for He. This means that 1 out of 5 collisions with water vapor, 1 out of 10 with nitrogen, 1 out of 33 with argon, and 3 out of 1000 with helium, are quenching collisions. This explains why at low pressures nitrogen is better than argon in increasing the thallium fluorescence as found by Loria and why water vapor is better



than nitrogen for developing the "for bidden" line 2656 as found by Wood and Gaviola.

The efficiency curve for  $H<sub>2</sub>$  ought to be a horizontal line since no collisions of the 6rst kind can be expected in this case. Fig. 6 shows that this is actually the case.

If we plot now the efficiency curve for CO we obtain a surprising result (Fig. 6); CO has a higher quenching efficiency than hydrogen and the extrapolated value for zero pressure is 2.5.

Table I gives in the second column the radii used; in the third column, the number of collisions Z obtained by formula (7) assuming a radius  $r =$  $2.91 \times 10^{-8}$  cm for the excited mercury atom, and in the fourth the efficiencies

obtained from Figs. 4, 5, and 6, extrapolating to zero pressure. Ke shall refer presently to the two last columns.

## THE CASE OF CO

In the case of CO we find the surprising result that the efficiency of quenching collisions increases far beyond 1 as the pressure diminishes and it approaches a value 2.5 for  $p=0$ . For the calculation of this curve we have used  $r_{\infty} = 1.6 \times 10^{-8}$  cm as radius of the CO molecule as given by Landolt-Börnstein and  $r_{\text{Hg}} = 2.91 \times 10^{-8}$  cm for the excited mercury atom as obtained

<sup>&</sup>lt;sup>14</sup> See for example T. Asada, R. Ladenburg and W. Tietze, Phys. Zeits. 29, 549 (1928).

<sup>\*</sup>Note added in proof. In a recent paper by M. L. Pool (Phys. Rev. 33, <sup>22</sup> (1929)) the existence of this effect has been shown in a more direct way.

in a former paragraph. Since an efficiency can not, by definition, be greater than 1 it is necessary to find an explanation for this result. Now the radius 1.62-fold normal attributed to the excited mercury atom was calculated under the assumption that the efficiency of  $hydrogen$  collisions was equal to 1. This assumption was arbitrary and it was made because hydrogen seemed so far to have the greatest quenching efficiency, which, as we see now, is not the case: actually CO has a greater quenching efficiency than  $H<sub>2</sub>$ . If we define now the efficiency of CO collisions as unity we must assume

TABLE I. The quenching efficiencies of various gases for the resonance radiation of Hg as calculated from two values of the radius of the excited Hg atom.

Gas	Radius	$Z(r_{\text{Hg}} = 2.91 \text{A})$ Efficiency	$\rightarrow 0$	$Z(r_{\rm Hg'} = 5.5{\rm A})$	Efficiency
н. $_{\rm H_2O}$ $\mathrm{N}_2$ He ററ	$1.09\times10^{-8}$ cm 1.36 $\times$ " " $1.58\times$ " $\mu$ 1.43 $\times$ " 1.00 $\times$ " $\mu$ $1.6 \times$ "	3.0 $\times$ 10 <sup>+7</sup> b 1.17 $\times$ " $1.05\times$ " $0.85 \times$ " $2.8 \times$ " 1.07 $\times$ " и	0.2 0.1 0.03 0.003 2.5	$8.16\times10^{+7}$ p $3.0 \times$ " $2.6 \times$ " $\alpha$ 2.16 $\times$ " $7.7 \times$ " 2.64 $\times$ " - 44	0.4 0.08 0.04 0.01 0.001

that the radius of the excited mercury-atom is larger than the one used before; a radius equal to  $5.5 \times 10^{-8}$  cm, which is about three times the radius of the normal atom gives us in fact an efficiency equal to 1 for CO. This radius is about twice as large as the one calculated in the case of  $H_2$ . If we assume that the radius  $5.5 \times 10^{-8}$  cm is the *real* radius of the excited mercury atom we must conclude that the efficiency of hydrogen collisions is less than one-half and accordingly diminish the efficiencies of the other gases. The two last columns of Table I are calculated under this assumption. But this conclusion is arbitrary: the collision section of the excited mercury atom may be different for each particular gas. The experiments give us only a value for the product  $E_1Z$  (See formula (2)) where Z is the number of collisions and  $E_1$  the efficiency of them, and Z is proportional to  $\sigma^2$  (formula 7) if  $\sigma$  is the sum of the radii of the two colliding molecules. We measure then the product  $E_1 \sigma^2$  and in order to calculate the radius sum  $\sigma$  we make an arbitrary assumption about  $E_1$  for one particular gas and then apply this value  $\sigma$  to all the other gases and calculate their efficiencies. This was the course followed by Stuart and by the author in the former calculations. But we could also do the contrary: we could assume  $E_1 = 1$  for all the gases and calculate a collision-section for each of them, but if we do so we obtain for gases like  $N_2$ , A, and He, collision sections many times smaller than the gas kinetic ones which is undesirable to assume. In these cases therefore we must assume  $E_1$ <1. But in the cases of  $H_2$  and CO (and perhaps  $O_2$ ) where assuming  $E_1=1$  the collision section turns out to be greater than the gas kinetic one, there is no need and there is not purpose in postulating  $E_1 < 1$ . An efficiency smaller than one would simply mean a still larger collision section. We can in these cases assume a different radius of the excited atom for each particular gas.

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It seems of course desirable to assume one radius for the excited atom as we have one for the normal atom and to express the different behavior of gases in terms of efficiency-coefficients, but we have seen the danger of such an assumption; we may always find a new type of collision in which the efficiency appears to be greater than 1, which would oblige us to increase the assumed radius and parallel with it to decrease all the efficiency coefficients for the other gases.

The simplest way seems then to maintain the gas kinetic radius of the normal also for the excited atom in all the cases in which doing so, the efficiencies turn out to be smaller than one, and when not, to assume a radius for the excited atom, larger than the gas kinetic one, for each particular case, so that the efficiencies in each case are unity. Table II is calculated this way. This assumption is of course also arbitrary.

Gas	Radius	$r_{\rm H\alpha'}$		Efficiency
н. Нe	$1.6 \times 10^{-8}$ cm $\mu$ $\mu$ $.09\times$ $\mu$ $\mu$ 1.36 $\times$ $1.58\times$ $\mu$ $\mu$ 1.43 $\times$ $\mu$ $\alpha$ $.00\times$	5.5 $\times$ 10 <sup>-8</sup> cm - 11 - 11 $2.91\times$ $\alpha$ $1.80\times$ и $1.80\times$ $\alpha$ $\mu$ $.80\times$ $\mu$ $\mu$ $.80\times$	2.7 $\times$ 10 <sup>+7</sup> <i>b</i> $3.0 \times$ " и $0.64\times$ -44 $0.6 \times$ - 66 - 44 "	0.05 0.006

TABLE II. Quenching efficiencies of various gases for the resonance radiation of  $Hg$ .

The results of the present investigation make necessary a revision of Foote's theory and on the other hand allow us to predict the life and the number of metastable atoms as a function of the foreign gas pressure under different conditions, all of which will be dealt with in one or two subsequent papers, which will appear shortly.

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