

THE QUENCHING OF MERCURY RESONANCE RADIATION
BY FOREIGN GASES*

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ABSTRACT

The intensity of emitted resonance radiation from Hg vapor is decreased as the pressure of an admixed gas increases. The following cycle of transitions occurs for the rare gases or nitrogen. Absorption of $\lambda 2537$ produces 3P_1 Hg' atoms. Some of these return to the $1S_0$ state by radiating and a portion of this radiation escapes to be observed as resonance. The rest is reabsorbed in the vapor producing more 3P_1 atoms. Some of the 3P_1 atoms undergo collision of the second type with foreign gas molecules resulting in 3P_0 atoms. A large fraction of these atoms return to the 3P_1 state by collision of the first type with high speed gas molecules. At 18°C one collision in 6000 satisfies the condition of conservation of energy and momentum requisite to such an energy transfer. Other 3P_0 atoms return to the normal state through collision with traces of hydrogen impurities in which the energy of the mercury atom is utilized in the dissociation of H_2 . Still other 3P_0 atoms collide with normal Hg atoms producing Hg₂' excited molecules. This cycle of transitions is completely developed from kinetic theory considerations in which every collision, except in the molecular formation, is considered as effective. All the constants may be computed directly. Concentrations of the 3P_0 state as high as one part in a few hundred may be readily obtained under moderately intense illumination.

THE intensity of the resonance radiation from mercury vapor at room temperature, excited by a resonance lamp, rapidly diminishes as the pressure of an admixed gas is increased.¹ A quantitative interpretation of the processes occurring, however, has heretofore not been very satisfactory. In connection with some work on fluorescence and photo-ionization of mercury vapor which the writer has in progress, it was necessary to consider more carefully the mechanism of the resonance quenching.

Hydrogen is especially effective for quenching mercury resonance, a pressure of about 0.2 mm being sufficient to reduce the intensity of the $\lambda 2537$ emission to one-half its value without the foreign gas. A normal mercury atom absorbs a quantum of the incident $\lambda 2537$ radiation and if, during its life in the 2^3P_1 state it collides with a hydrogen molecule, the latter is dissociated. The energy otherwise available for radiation is used mainly in the work of dissociation, the small amount of energy remaining over going into kinetic energy, for the most part, of the hydrogen atoms. From simple kinetic theory, one may compute the pressure p of the admixed gas which is necessary in order that the probability of a collision between a 2^3P_1 atom and a gas molecule be equal to the probability that the excited

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¹ Stuart, *Zeits. f. Physik.* **32**, p. 262 (1925).

Cario and Franck, *idem* **37**, p. 619 (1926).

Hg atom radiates during the mean life $\tau = 1.1 \cdot 10^{-7}$ sec. in the undisturbed state, as follows:

$$p = \frac{3.84 \cdot 10^{-23}}{\sigma^2 \tau} \left(\frac{M_1 M_2}{M_1 + M_2} \right)^{1/2} \quad (1)$$

In this equation p is the pressure in mm Hg, M_1 , the molecular weight of Hg, M_2 that of the foreign gas, and σ the sum of the radii of the two colliding molecules, the temperature being 18°C . Assuming every collision effective in quenching, and that this is the only effect of the foreign gas, and neglecting the absorption, within the resonance bulb, of the emitted resonance radiation, Eq. (1) should give the pressure at which the intensity of the resonance radiation is reduced to half its value without the admixed gas. Actually, these assumptions require considerable modification.

The statistical processes occurring in the quenching by H_2 may be illustrated by Fig. 1a. The number of transitions per sec. from 1^1S_0 to 2^3P_1

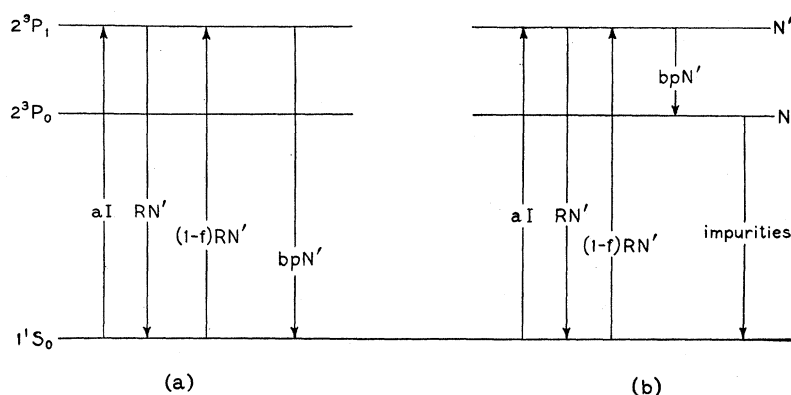


Fig. 1. (a) Quenching by H_2 . (b). Analogous diagram for quenching by rare gases.

is equal to a constant a times the intensity I of the incident monochromatic illumination. This assumes that the added gas does not seriously change the amount of energy absorbed by the resonance cell. In the first place, the Lorentz broadening of the absorption line at gas pressures ranging from zero to one or two hundred mm Hg, is certainly small compared with the Doppler broadening and especially to the coupled damping influence² of the other Hg atoms to which the vapor is astonishingly sensitive. Direct experiments on the Lorentz broadening are performed at pressures of many atmospheres where the effect becomes measurable. Secondly as the absorption line is broadened, the absorption coefficient at the maximum decreases so that with a source representing a constant spectral distribution, the relative increase in total absorbed energy is less than the relative increase in Lorentz broadening. Finally in Stuart's experiments, the source was itself a resonance lamp and the resonance cell was deep enough to absorb all the energy incident

² Holtsmark, Zeits. f. Physik. **34**, p. 722 (1925). Trumpy *idem*. **34**, p. 715 (1925); **40**, p. 594 (1926).

upon it. Merely the depth of penetration should be therefore increased slightly by the foreign gas while the total number of quanta absorbed remains unchanged. Accordingly, in any of the ordinary resonance experiments, it does not appear necessary to consider a as a function of the pressure although this could be readily done if desired.

Some of the atoms in the 2^3P_1 state radiate, and the number of radiating transitions is equal to a constant R times the population N' of the 2^3P_1 level. Other Hg' atoms collide with H_2 molecules, the number of such transitions being the product of a constant b , the pressure p of the added gas, and the population N' . Of the total RN' quanta emitted by the vapor per sec., let the fraction f escape from the bulb as resonance radiation while the amount $(1-f)RN'$ is reabsorbed. Then for equilibrium we have

$$aI + (1-f)RN' = RN' + bpN'. \quad (2)$$

The intensity J of the resonance radiation is proportional to fRN' ; let $fRN' = gJ$ where g is a constant. On choosing the scale for intensity of resonance such that $J=100$ when $p=0$, we obtain from Eq. (2)

$$J = 100 / (1 + bp/fR) \quad (3)$$

for the relation between the intensity of the resonance radiation and the pressure of the admixed H_2 . Stuart's data at $18^\circ C$ furnish an empirical evaluation of $b/fR = 4.6$. Using this constant, the J vs. p relation is plotted in Fig. 4, according to Eq. (3) while the dots represent the observations.

At a pressure such that $bp/fR = 1$ (i.e., $p = 0.217$ mm) the resonance radiation is reduced to half its initial value while at a somewhat greater pressure $p = 0.217/f$, where $bp/R = 1$, there is equal probability that a Hg' atom radiates or collides with a H_2 molecule. This latter pressure, and hence f , could be computed directly from Eq. (1) if the effective radius of the Hg' atom were known. However, the quantity f may be estimated in another manner. In Stuart's experiments the radiation was directed on one face of the resonance cell and the intensity of radiation emitted back through the same face in a direction nearly symmetrical to the incident beam was measured photographically. Let $E = E_0 e^{-\mu x}$ be the energy flux at any depth x along the beam within the resonance cell. The rate of absorption of energy at the point x is accordingly $dE = \mu E_0 e^{-\mu x} dx$. The rate at which the absorbed energy returns from this point to the front of the cell is $K dE e^{-\mu x}$ where K is a constant depending on the geometry of the apparatus. Integrating this from $x=0$ to ∞ one obtains $0.5KE_0$. If there had been no absorption on the way out, the escaping energy rate would have been KE_0 . A second approximation for f involves consideration of the secondary resonance excited by the primary emission, but this first approximation appears sufficiently accurate for the present. As will be evident later, the only error introduced in the following discussion by an incomplete evaluation of f is of a differential nature arising in the fact that the kinetic theory radii of various gases differ slightly.

Using $f=0.5$, the hydrogen pressure for equal probability of radiation or impact is 0.434 mm. Substituting this in Eq. (1) and assuming the kinetic theory radius for H_2 ($\sigma_1=1.34 \cdot 10^{-8}$) we obtain $\sigma_2=2.03 \cdot 10^{-8}$ cm for the radius of the Hg' atom. The kinetic theory value for the unexcited atom Hg is $1.75 \cdot 10^{-8}$ which is somewhat smaller than the above computed radius, as should be expected. With $\sigma_2=2.03 \cdot 10^{-8}$ and the accepted kinetic theory radii for the foreign gases one may compute by Eq. (1) the value of the constant b/R , the reciprocal of which is numerically equal to the pressure in mm at which there is equal probability for the Hg' atom to radiate or to collide. These data are summarized in Table I.

TABLE I
Kinetic theory data.

Gas	Radius	Type of collision	b/R	b/fR
Hg	$1.75 \cdot 10^{-8}$	$Hg'-Hg$	0.41	0.82
H_2	1.34	$Hg'-H_2$	2.3	4.6
N_2	1.90	$Hg'-N_2$	0.89	1.78
He	1.11	$Hg'-He$	1.42	2.84
A	1.81	$Hg'-A$	0.74	1.48
Hg'	2.03			

Quenching by gases which have no critical potential below the 4.9 volt point of mercury takes place in a manner different from that described for H_2 . At collision the 2^3P_1 atom drops to the 2^3P_0 metastable state giving up an energy equivalent to 0.218 volts which is dissipated mainly as kinetic energy of the lighter foreign gas molecule. The number of such transitions occurring per sec. is bpN' as shown in Fig. 1*b*. It has always been assumed that at room temperature no appreciable number of reverse transitions from 3P_0 to 3P_1 occurs; hence the quenching should not be concerned with the population N of the former state. It is sufficient that the slightest trace of impurity such as H_2 will prevent an extremely high concentration of this long-lived metastable state through collisions leading to dissociation. The relation between J and p therefore should be of the form given by Eq. (3).

If this relation is applied to Stuart's data, the values of fR/b increase very rapidly with the pressure as shown in Fig. 2. It seems quite reasonable that the small values of fR/b , which the curves tend to approach at low pressure (not distinguishable from zero on the large scale of this figure), are the kinetic theory constants as given in Table I. Stuart considered only the constant at the pressure corresponding to 50 percent quenching and finding that the experimentally observed pressures were up to 300 times those computed by Eq. (1), concluded that each gas possessed an efficiency coefficient for an effective quenching collision. The variation of these coefficients, however, is much more marked for the same gas at different pressures. Thus, if we adopt this interpretation, the coefficient for helium varies from 0.00054 at 230 mm to values approaching unity near zero pressure. The form of the curves of Fig. 2 suggests that the collisions are

always effective but that another process is occurring which partially offsets the rapid quenching on the basis of 100 percent efficiency. This process consists in the upward transitions $^3P_0 \rightarrow ^3P_1$ produced by collisions between the metastable Hg' atoms and fast gas molecules.

In a mixture, therefore, of two gases, Hg' and the foreign gas, it is necessary to know the fractional number of collisions between the two different types of molecule for which the available kinetic energy is sufficient to effect the transition $^3P_0 \rightarrow ^3P_1$. We shall omit consideration of the change in angular

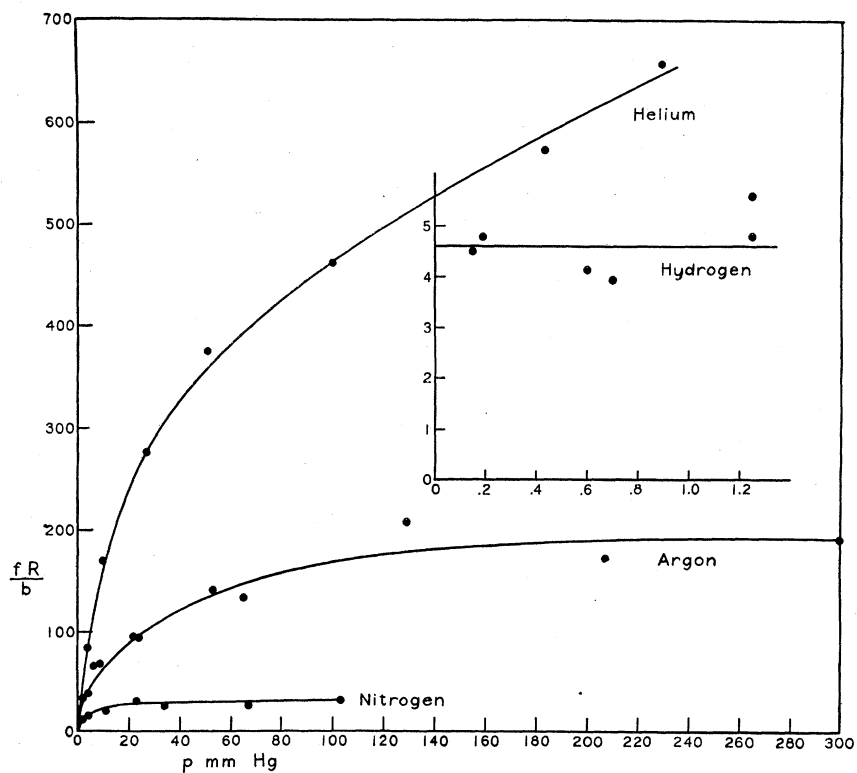


Fig. 2. Values of fR/b on scheme shown by Fig. 2b.

momentum of the Hg' atom and, as is customary in problems connected with the kinetic theory of chemical reactions, shall assume that only the component of the relative velocity of the two impacting atoms, resolved along the line of centers, is effective. The total number of all collisions per sec. between the two different kinds of molecule, n_1 of absolute mass m_1 and n_2 of mass m_2 is given³ by Eq. (4)

$$\text{Total number of collisions per sec} = 2\sigma^2 n_1 n_2 \left[\frac{2\pi kT(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \quad (4)$$

³ This equation and Eq. (5) are derived in detail by Tolman, Statistical Mechanics, p. 69, Chemical Catalog Co.

where $k = 1.372 \cdot 10^{-16}$ erg deg $^{-1}$. The fractional part F of these in which the component of relative velocity parallel to the line of centers is greater than R_0 is

$$F = e^{-\frac{m_1 m_2}{m_1 + m_2} \frac{R_0^2}{2kT}}. \quad (5)$$

Let ϵ_0 = the energy difference between the 3P_0 and 3P_1 energy levels, i.e., $3.47 \cdot 10^{-13}$ ergs corresponding to 0.218 volts. In order that conservation of energy and linear momentum obtain, the collision must be subject to the condition

$$R_0^2 = 2\epsilon_0(m_1 + m_2)/m_1 m_2. \quad (6)$$

Substituting this in Eq. (5) we find

$$F = e^{-x} \text{ where } x = \epsilon_0/kT. \quad (7)$$

The fractional number of collisions capable of effecting the upward transition $^3P_0 \rightarrow ^3P_1$ is therefore independent of the nature of the added gas.

The application of Eq. (7) furnishes an interesting picture for the quantum theory distribution of excited states. For example, consider the atoms belonging to Group III of the periodic table where we have two low-lying metastable 2P terms. Assume n atoms in the normal state and m in the higher level. The number of transitions per sec. from n to m is $Fb_p n$, where Fb_p represents the collision rate with fast atoms, while the number of transitions from m to n equals $b_p m$. Equating for equilibrium, we find $m/n = F = e^{-x}$ where $x = \epsilon_0/kT$ in agreement with the ordinary quantum theory derivation. Indeed, it might have been more logical to have approached the problem solely from this standpoint thus avoiding the question of what constitutes an effective collision.

Values of F for several temperatures are as follows:

t°C:	18	20	25	750
F:	0.000168	0.000177	0.000206	0.0846

Thus at 18°C, out of every 6000 collisions there is one in which the transfer of kinetic energy is sufficient to produce the transition from 3P_0 to 3P_1 . Hence, if the life of the metastable state, which is terminated by collision with impurities, etc., were 6000 times that of the 3P_1 state⁴ the probability that a 3P_0 atom collides with a high speed gas molecule should be the same as the probability that a 3P_1 atom makes any collision at all. It is therefore surprising that the importance of such upward transitions at room temperature has not been realized, especially in view of the work by Cario and Franck who found no quenching at 750°C where about one collision in twelve involves the requisite energy.

Every time a 3P_0 atom is lost by collision with an impurity a small amount of kinetic energy is communicated to the body of the gas, 0.218 volts in the transitions $^3P_1 \rightarrow ^3P_0$ and whatever energy remains after the dissociation process. The high speed molecules so produced, however, are directly ineffective. For example, at 10 mm gas pressure, a mercury pressure

⁴ Experimental determinations frequently indicate a much longer life. Cf. Dorgelo, *Physica* 5, p. 492 (1925).

of 0.0015 corresponding to 18°C , and an assumed concentration of 3P_0 atoms of 0.1 percent, any individual high speed gas atom on the average would make roughly twenty million collisions with other gas atoms before encountering a 3P_0 atom. During this time the Maxwellian distribution of velocities should be accurately established. Hence, such transitions result only in increasing the temperature of the gas by an amount which the writer found too small to be easily detected; certainly not enough to alter appreciably the value of F in the usual resonance radiation experiments.

If N be the population of the 3P_0 state, the product of a constant d , the pressure p , and N , represents the number of upward transitions occurring per sec. at a given temperature. In order to eliminate N from the relations it is necessary to know by what other processes the supply of 3P_0 atoms is exhausted. It has been generally assumed by Franck and his colleagues that collision between an excited and normal Hg atom results in a Hg_2' excited molecule. The number of such transitions may be represented by cN where c is a constant proportional to the pressure of Hg vapor. That such a process actually occurs is not definitely established. Probably there is no better evidence for its existence than the fact that it yields consistent results in the following derivation. The writer has some indirect evidence from work on fluorescence, with very intense illumination, that molecules consisting of two excited atoms may play a rôle in these quenching processes but for the present we shall assume that the probability of the collision of two excited atoms is small compared with that of an excited and normal atom, *a priori* an almost obvious conclusion since the concentration of excited atoms is small. A further important loss from the 3P_0 state is produced by a trace of impurity such as hydrogen. Thus at 10 mm gas pressure an impurity of a few parts in 10^5 should be as effectual in quenching by dissociation as

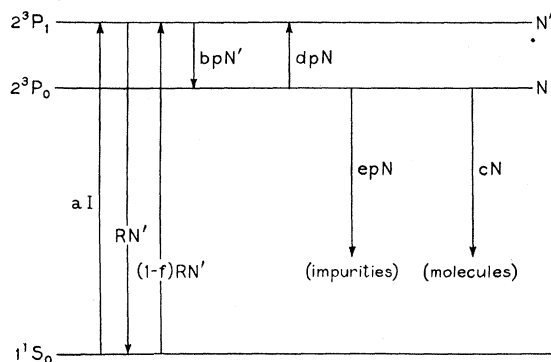


Fig. 3. Complete scheme for quenching by rare gases.

is the mercury vapor in quenching by molecular formation, assuming as usual 100 percent efficiency in all processes. The impurity loss may be represented by epN where e involves the ratio of the pressures of the impurity and of the gas as well as the collision rate. Small impurities have no effect on the 3P_1 state because of its short life.

The transition diagram for quenching by the rare gases, as discussed above, is shown in Fig. 3. Equating the number of transitions to and from each level, we obtain

$$aI + (1-f)RN' + d\dot{p}N = b\dot{p}N' + RN' \quad (8)$$

$$b\dot{p}N' = d\dot{p}N + cN + e\dot{p}N. \quad (9)$$

On eliminating N from these equations, putting $fRN' = gJ$, and letting $J=100$ when $\dot{p}=0$ one finds

$$J = \frac{100}{\left[1 + \frac{\left(\frac{c}{d\dot{p}} + \frac{e}{d} \right) b\dot{p}}{fR} \right] \left(1 + \frac{c}{d\dot{p}} + \frac{e}{d} \right)} \quad (10)$$

This relation may be rectified by plotting the reciprocal of

$$\frac{b/fR}{(100/J) - 1} - \frac{1}{\dot{p}}$$

versus the pressure \dot{p} . The slope of the straight line so obtained gives the value of e/d , and the intercept when $\dot{p}=0$, the value of c/d . The first four columns of Table II summarize the constants for three gases based on

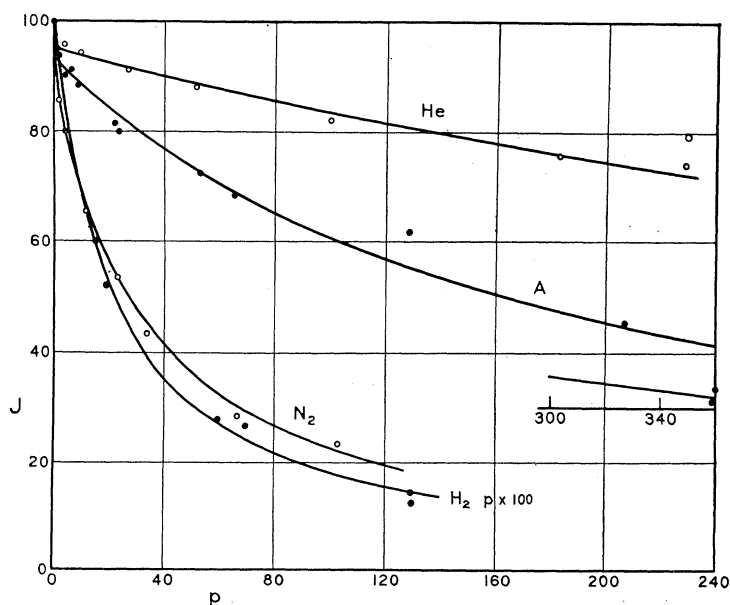


Fig. 4. Quenching by several gases. The full lines are drawn according to the theory and the plotted points represent Stuart's observations.

Stuart's data. In Fig. 4 the full lines are drawn in accordance with Eq. (10) while the plotted points represent the observations. No point deviates from the curves by more than the experimental error.

TABLE II
Quenching data.

Gas	c/d	e/d	b/fR	Impurity (H ₂) 1 part in	c/d computed
He	.0180	.00051	2.84	18,000,000	2.6
N ₂	.060	.0193	1.78	800,000	4.1
A	.050	.0039	1.48	4,900,000	5.1

It is possible to estimate the amount of impurity, considered as H₂, which was present in Stuart's experiments. The quantity epN represents the collision rate with the impurity at the pressure p' while dpN is the collision rate with fast gas atoms at the pressure p . Eq. (4) may be rewritten as follows:

$$\text{collision rate} = A p \sigma^2 [(M_1 + M_2)/M_1 M_2]^{1/2}$$

where A is a constant for a given temperature. Hence

$$Hg' - gas \quad dpN = A F_{18} p \sigma^2 [(M_1 + M_2)/M_1 M_2]^{1/2}$$

$$Hg' - H_2 \quad epN = A p' (8.0) 10^{-16}$$

$$\frac{p'}{p} = \frac{e}{d} \frac{F_{18} \sigma^2 [(M_1 + M_2)/M_1 M_2]^{1/2}}{8.0 \cdot 10^{-16}} \quad (11)$$

On substituting the values for the constants and determining σ from the data in Table I, the relative H₂ contents shown in column 5 of Table II are obtained. These values may not be unreasonable. One should expect high purity as indicated since special precautions were observed in handling the gas and especially since the radiation should exert a clean-up action.

It is especially interesting that the computed impurity in N₂ is at least as small as that likely to have been present. According to spectroscopic data the N₂ molecule is capable of absorbing vibrational energy in almost any amount up to several volts. Quenching of the ³P₀ state by such a process and the ultimate distribution of this energy as kinetic energy, since the vibrational states are radiationless, would be interpreted, in accordance with Fig. 3, simply as the effect of an impurity. We may therefore conclude that collisions in which the ³P₀ (or ³P₁) atom transfers energy to a vibrational state of the N₂ molecule are improbable. This may be also inferred from the fact that, according to Cario and Franck, there is no quenching of the ³P₁ state at 750°C.

The constant c/d possesses significance from the kinetic theory standpoint. We have: cN = rate of collision between Hg' and Hg normal atoms at pressure 0.0015 mm while dpN = rate of collision between Hg' and fast

gas molecules at pressure p . Whence by the same procedure as that used in deriving Eq. (11) one obtains

$$\frac{c}{d} = \frac{0.00215 \cdot 10^{-16}}{F_{18} \sigma^2 [(M_1 + M_2)/M_1 M_2]^{1/2}}. \quad (12)$$

Values of c/d so computed are given in column 6 of Table II. These are roughly 100 times the empirically determined constants. That the computed collision rate c should exceed the experimental data for molecular formation is precisely what may be expected from our knowledge of chemical reactions. As discussed by Tolman⁵ no bimolecular reaction rate is known which even approaches the kinetic theory value. In the recombination of monatomic bromine one collision in about 1250 is effective, an efficiency of 0.1 percent. The reaction efficiency for the Hg_2' molecular formation of about 1 percent is therefore perhaps the highest efficiency yet observed for a bimolecular reaction. Such efficiencies may be interpreted as the result of an essential orientation of the colliding atoms but since nothing regarding the process is understood, we shall in the following discussion employ the empirical values of c/d as experimental facts.

The relative populations of the 3P_0 and 3P_1 levels may be determined by use of Eq. (9).

$$\frac{N}{N'} = \frac{b}{d} \frac{p}{p + \frac{c}{d} + \frac{e}{d}p}. \quad (13)$$

The quantity d/b is simply the fractional number of collisions between 3P_0 atoms and gas molecules in which the available kinetic energy is sufficient to effect the transition $^3P_0 \rightarrow ^3P_1$; that is $b/d = 1/F = 5950$ at 18°C . Thus for N_2 at the pressure p we find

$$N/N' = 5950p/(1.02p + 0.06). \quad (14)$$

The population ratio at 18°C is accordingly zero at zero pressure, rising rapidly within 1 or 2 mm gas pressure where it practically reaches the asymptotic value 5800. The intensity of the resonance radiation is proportional to the population N' and decreases with increasing pressure as shown by Fig. 4. Hence the population N of the metastable level rapidly increases from zero to a maximum at 1 or 2 mm (depending of course upon the impurity content) and then falls at approximately the same rate as the resonance radiation.

The data permit the evaluation of the mean life of the Hg' atom. Let t' be the mean life of the 3P_1 state. The population N' is equal to t' times the rate at which transitions occur to or from this state, or from Fig. 3:

$$N' = t'(RN' + bpN') \quad (15)$$

⁵ Loc. cit., p. 242.

and

$$t' = \frac{1/R}{1 + bp/R} \quad (16)$$

But when $p=0$, $t'=\tau=1.1 \cdot 10^{-7}$ sec. so that $1/R=1.1 \cdot 10^{-7}$ and fR , to be used later, is equal to $4.54 \cdot 10^6$. Hence with N_2 gas present $t'=1.1 \cdot 10^{-7}/(1+0.89p)$. Thus the mean life t' with a moderate gas pressure may differ from τ by several orders of magnitude, a fact not always recognized. At 2 mm N_2 the life is $4 \cdot 10^{-8}$ sec.

Let t be the mean life of the 3P_0 state. The rate of supply for this state is bpN' . Accordingly $bpN't=N$ and

$$t = \frac{N}{N'} \cdot \frac{R}{b} \cdot \frac{1}{R} \cdot \frac{1}{p} \quad (17)$$

Thus for 2 mm N_2 the life of the metastable state is $t=3.5 \cdot 10^{-4}$ sec at 18°C , and for higher pressure the life is approximately inversely proportional to p .

If we knew the rate at which the Hg vapor absorbed quanta under a given stimulation it should be possible to estimate the actual concentrations of the 3P_0 and 3P_1 atoms. Precise measurements of this type are greatly needed. Qualitative observations made by the writer with the direct illumination from a water-cooled arc indicated that about 0.01 watt of $\lambda 2537$ was absorbed by 10 cm³ of Hg vapor at 18°C , corresponding to $1.3 \cdot 10^{16}$ quanta/sec. In this amount of vapor there are $5 \cdot 10^{14}$ Hg atoms. Such illumination may be several hundred times that employed by Stuart but is probably of much less intensity than that used by Wood⁶ in his experiments on "controlled orbital transitions." We shall see that the simple theory so far developed is not precisely applicable for such intense illumination but qualitatively it shows that very high concentrations of the metastable state are possible. It readily follows from Eqs. (8) and (9) that

$$N' = \frac{aI}{fR \left[1 + \frac{bp}{fR} \frac{\frac{c}{d} + \frac{e}{d}p}{p + \frac{e}{d}p + \frac{c}{d}} \right]} \quad (18)$$

where $aI=1.3 \cdot 10^{16}$ quanta/sec. and all the constants are known. At 2mm N_2 we find $N'=2.45 \cdot 10^9$ and by Eq. (14) $N=1.39 \cdot 10^{13}$. Since there are $5 \cdot 10^{14}$ Hg atoms, 1 atom in 204,000 is in the 3P_1 state and 1 atom in 36 is in the 3P_0 state. With so high a concentration of the 3P_0 state, collisions between metastable atoms become of importance and an additional loss hN^2 must be considered in the cycle of Fig. 3. The relations existing under high illumination will be discussed in a later paper in connection with fluorescence phenomena.

⁶ Wood, Phil. Mag. 50, p. 774 (1925).

Confining our attention to moderate illumination, the ratio of the number of downward to upward transitions bpN'/dpN produced by collision is of interest. From Eq. (13) it follows that

$$\frac{bpN'}{dpN} = 1 + \frac{e}{d} + \frac{c}{dp} \quad (19)$$

On substituting the values for the constants, one finds that, with N_2 at 2 mm, out of every 100 downward transitions 95 go back by collision with high speed molecules and 98 go back at a pressure of 100 mm. From Eqs. (8) and (13)

$$\frac{aI}{dpN} = \left(1 + \frac{e}{d} + \frac{c}{dp}\right) \left(1 + \frac{fR}{bp}\right) - 1 = 0.343 \text{ for } p = 2\text{mm}N_2 \quad (20)$$

Hence the number of transitions upward may exceed by far the total number of incident quanta because of the many transitions occurring back and forth between the 3P_1 and 3P_0 levels. As a specific example, we may consider 1000 incident quanta absorbed by the bulb of Hg vapor per sec. and a N_2 pressure of 2 mm. The following numerical values, corresponding to Fig. 3, are then obtained by the use of the formulas already given.

$N_2 p = 2 \text{ mm}$	$bpN' = 3060$	$epN = 57$
$Hg p = 0.0015 \text{ mm}$	$J = fRN' = 855$	$cN = 88$
$aI = 1000$	$RN' = 1710$	$N' = 0.0002$
$dpN = 2915$	$(1-f)RN' = 855$	$N = 1.07$

With incident radiation supplied at the rate of 1000 quanta per sec., 1710 quanta are emitted by the vapor of which 855 escape as resonance radiation. There are 3060 collisions which result in the transition $^3P_1 \rightarrow ^3P_0$ and 2915 collisions in which the reverse process occurs. Hg_2' molecules are formed at the rate of 88 per sec. and 57 H_2 molecules, present as impurities, are dissociated. One five-thousandth of an atom represents the population of the 3P_1 level and one atom that of the 3P_0 level. Similar computations may be made for other pressures and for different admixed gases.

Attention should be directed to the fact that a normal Hg atom is effective in performing the transition $^3P_1 \rightarrow ^3P_0$; hence, if the present discussion were applied to experiments in which the Hg pressure were materially increased, the effect of such collisions should not be neglected. Also in considering the quenching due to Hg vapor alone, the variation of the absorption probability a with pressure becomes of great importance on account of the strong influence of coupled damping.

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