THE QUENCHING OF MERCURY RESONANCE RADIATION BY FOREIGN GASES

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ABSTRACT

Milne's Theory of the diffusion of imprisoned resonance radiation is applied to Stuart's experiments on the quenching of Hg resonance radiation by foreign gases, and expressions obtained for n_2, the number of excited Hg atoms per cc, and J, the quenching, in terms of k, the number of impacts of the second kind per sec per excited atom. Stuart's experimentally determined values of J are used to give the relation between k and the pressure of the foreign gas, and the result is obtained that the number of impacts of the second kind per sec per excited atom is not a constant fraction of the total number of collisions. The total number of impacts of the second kind per cc is calculated and taken as the reaction velocity, and upon plotting against the pressure it is shown that the reaction velocity varies as the 0.6 power of the pressure for all the foreign gases. It is shown how these results can be explained on the theory that impacts between excited Hg atoms and foreign gas molecules give rise to metastable Hg atoms, which diffuse to the incident wall and meet there adsorbed foreign gas molecules to which they give up their energy. This theory is also capable of explaining the behavior of a large quantity of inert gas on the dissociation of hydrogen and oxygen by excited Hg atoms.

INTRODUCTION

IF LIGHT from a Hg resonance lamp at room temperature is incident on a face of another Hg resonance lamp containing a foreign gas, the secondary resonance radiation is quenched by an amount depending on the pressure of the foreign gas.[1,2,3] The relation between the re-emitted resonance radiation, J, and the pressure of the foreign gas, p, called the quenching curve, was obtained and plotted by Stuart for a number of gases among which were O_2, H_2, CO_2, H_2O, N_2, A and He. On the assumption that the resonance radiation is reduced to one half its original value when the probability of an impact between an excited Hg atom and a foreign gas molecule equals the probability that an excited Hg atom will radiate, and upon assuming the radius of an excited Hg atom to be about three times the normal value, Stuart was able to compute the "efficiency" or "yield" of impacts of the second kind. These values varied widely among themselves—being 100% for O_2, 70% for H_2, and about 0.03% for He, the values for the other gases being between these limits. If the radius of an excited Hg atom is taken larger, the efficiencies are reduced, but the general order among the different gases remains the same. The high quenching efficiency of hydrogen is usually explained on the basis that, since it requires only 4.3 volts to dissociate a hydrogen molecule, an excited Hg atom with an energy of 4.9 volts can perform this dissociation upon impact. This is in good agreement with the

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[1] Wood, Phys. Zeits. **13**, 353 (1912).

[2] Cario, Zeits. f. Physik **10**, 185 (1922).

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

experiments of Franck and Cario,[4] but several difficulties still remain. First, one would expect 100% efficiency for hydrogen on this point of view. If the radius of an excited Hg atom is chosen so as to give such an efficiency, however, the efficiency for oxygen comes out greater than 100%. Second, if a 4.9 volt excited Hg atom can dissociate a hydrogen molecule so easily merely because it has sufficient energy, one would expect a 4.9 volt electron, upon impact, to do the same. Hughes,[5] however, found no dissociation by electron impact even at 8.9 volts. Finally the high quenching efficiency of oxygen seems to have no explanation whatever.

Foote[6] recently attempted an explanation of Stuart's quenching curves from a point of view which differentiated sharply between the behavior of hydrogen and that of other gases. According to Foote, *all* impacts between excited Hg atoms and foreign gas molecules are of the second kind, but only in the case of hydrogen is the excitation energy of the excited Hg atom completely used up, partly in dissociating the hydrogen molecule and partly in kinetic energy, giving an efficiency of 100%. Impacts between excited Hg atoms and molecules other than hydrogen produce metastable Hg atoms which, upon further impacts, yield either excited Hg atoms once again, or Hg_2 molecules or, if an impurity is present, normal Hg atoms. Relations between J and p were deduced for the two different cases, and by choosing the unknown constants in these expressions to agree with Stuart's data, information was obtained about the number of metastable atoms, the rate of formation of molecules, and the concentration of impurities.

Foote does not mention, however, the anomalous behavior of oxygen, and although it is conceivable that a slight amount of hydrogen as an impurity might account for the quenching efficiencies of helium, argon and nitrogen, those of O_2, CO_2 and H_2O cannot be accounted for in this way. Moreover, his method of treating the absorptions and re-emissions of quanta of 2537 by Hg atoms was rather approximate, and it was thought worthwhile to apply Milne's theory[7] of imprisoned resonance radiation to this problem, since this theory, extended to include impacts of the second kind has been fairly successful in accounting for the persistance of imprisoned resonance radiation in Hg vapor.[8] In the present paper a relation between J and the number of impacts of the second kind per sec. per cc is obtained for all foreign gases on the basis of Milne's theory. We take into account the geometry of Stuart's apparatus and make only one assumption about the behavior of the foreign gas molecules, to wit: The number of impacts of the second kind per sec. per cc is proportional to the number of excited Hg atoms per cc, the proportionality factor being an unknown function of the pressure of the foreign gas or

$$\left.\begin{matrix}\text{Number of impacts of second}\\ \text{kind per sec. per cc}\end{matrix}\right\} = kn_2$$

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[4] Franck and Cario, Zeits. f. Physik **11**, 161 (1922); **17**, 209 (1923).

[5] Hughes, Phil. Mag. **41**, 778 (1921).

[6] Foote, Phys. Rev. **30**, 288 (1927).

[7] Milne, Journ. Lond. Math. Soc. Vol. I (1926).

[8] Zemansky, Phys. Rev. **29**, 513 (1927).

where n_2 is the number of excited Hg atoms per cc and $k=f(p)$ is the number of impacts of second kind per sec. per excited atom.

If the number of impacts of the second kind per sec. per excited atom were a constant fraction of the total number of impacts, then k would be equal to a constant times the pressure of the foreign gas. This is the assumption that has always been made. It is not necessary, however, to make any assumptions concerning k at this point, because Stuart's experiments themselves will furnish the functional relation between k and p.

MILNE'S THEORY

If a mass of gas be enclosed between two infinite planes at $x=-a$ and $x=+a$, and if isotropic, monochromatic radiation, for which the gas has the atomic absorption coefficient α, be incident on the face $x=-a$, then, it has been shown by Milne that the number of excited atoms per cc, n_2, is obtained by solving the differential equation

$$(\partial^2/\partial x^2)(n_2+\tau\partial n_2/\partial t)=4\alpha^2N^2\tau\partial n_2/\partial t \tag{1}$$

where τ is the life-time of the excited state, and N is the total number of atoms per cc. Also, the intensity of the radiation advancing in the positive x direction is

$$I_x=\frac{\sigma q_1}{Nq_2}\left[\left(n_2+\tau\frac{\partial n_2}{\partial t}\right)-\frac{1}{2\alpha N}\frac{\partial}{\partial x}\left(n_2+\tau\frac{\partial n_2}{\partial t}\right)\right]$$

and the intensity of the radiation advancing in the negative x direction is

$$I_x'=\frac{\sigma}{N}\frac{q_1}{q_2}\left[\left(n_2+\tau\frac{\partial n_2}{\partial t}\right)+\frac{1}{2\alpha N}\frac{\partial}{\partial x}\left(n_2+\tau\frac{\partial n_2}{\partial t}\right)\right] \tag{3}$$

where σ, q_1 and q_2 are constants with which we do not have to concern ourselves in this problem. In these equations, $\partial n_2/\partial t$ represents the total rate at which excited atoms are forming. To take into account the destruction of excited atoms, it is necessary merely to replace $\partial n_2/\partial t$ everywhere by $\partial n_2/\partial t+kn_2$ according to the assumption made above, and in order to apply the theory to the case of a cylindrical mass of gas, we have merely to transform the differential equation (1) into cylindrical coordinates.

THE PROBLEM

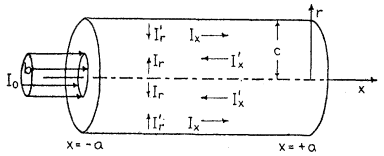

Fig. 1.

The conditions under which the present calculation is carried out are shown in Fig. 1. We have a cylindrical absorption cell of quartz containing N Hg atoms per cc, and a pressure, p, of some foreign gas. A circular portion, of radius b, of the face at $x=-a$ is bathed in radiation from a Hg resonance lamp at room temperature. The radius of the absorption cell is c and the length is $2a$. We wish to find the value of the backward radiation I_x' at the point $r=0$, $x=-a$ in the steady state $(\partial n_2/\partial t=0)$, the boundary conditions being

$$I_x'=0 \text{ when } x=+a,\ 0<r<c \tag{4}$$

$$I_r'=0 \text{ when } r=c,\ -a<x<+a \tag{5}$$

$$I_x=\begin{cases} I_0 \text{ when } x=-a,\ 0<r<b \\ 0 \text{ when } x=-a,\ b<r<c. \end{cases} \tag{6}$$

We have first to obtain the solution of the differential equation

$$\partial^2 n_2/\partial r^2+\partial n_2/r\partial r+\partial^2 n_2/\partial x^2=4\alpha^2N^2\tau k n_2/(1+\tau k) \tag{7}$$

subject to the conditions that

$$n_2+(1/2\alpha N)(\partial n_2/\partial x)=0 \text{ when } x=+a,\ 0<r<c. \tag{8}$$

$$n_2+(1/2\alpha N)(\partial n_2/\partial r)=0 \text{ when } r=c,\ -a<x<+a \tag{9}$$

$$n_2-(1/2\alpha N)(\partial n_2/\partial x)=\begin{cases} Nq_2I_0/\sigma q_1(1+\tau k) \text{ when } x=-a,\ 0<r<b \\ 0 \text{ when } x=-a,\ b<r<c \end{cases} \tag{10}$$

and then to calculate I_x' at $x=-a$, $r=0$.

The solution of (7) is found to be

$$n_2=\frac{2bNq_2I_0}{c^2\sigma q_1(1+\tau k)}\sum J_0(\mu_k r)\times \frac{\mu_k J_1(\mu_k b)\left[\cosh p_k(a-x)+(2\alpha N/p_k)\sinh p_k(a-x)\right]}{(4\alpha^2N^2+\mu_k^2)\left[J_0(\mu_k c)\right]^2\left[2\cosh 2ap_k+(2\alpha N/p_k+p_k/2\alpha N)\sinh 2ap_k\right]} \tag{11}$$

where $p_k=(4\alpha^2N^2\tau k/(1+\tau k)+\mu_k^2)^{1/2}$; $\mu_k=y_k/c$; and y_k is the Kth root of $2\alpha NcJ_0(y)\ =\ yJ_1(y)$. When there are no impacts of the second kind, $k=0$ and $p_k=\mu_k$ whence, without impacts of the second kind,

$$n_2=\frac{2bNq_2I_0}{c^2\sigma q_1}\sum J_0(\mu_k r)\times \frac{\mu_k J_1(\mu_k b)\left[\cosh\mu_k(a-x)+(2\alpha N/\mu_k)\sinh\mu_k(a-x)\right]}{(4\alpha^2N^2+\mu_k^2)\left[J_0(\mu_k c)\right]^2\left[2\cosh 2a\mu_k+(2\alpha N/\mu_k+\mu_k/2\alpha N)\sinh 2a\mu_k\right]} \tag{12}$$

In Stuart's experiments, $2a$ is 10 cm, c is about 2.5 cm, b about 1 cm, and $\alpha N=3$.[9] With these values, it is found that the smallest value of μ_k is about 1, whence $2a\mu_k$ and $2ap_k$ are at least 10, and cosh $2a\mu_k$ is very nearly equal to sinh $2a\mu_k$.

Eq. (12) enables us to see how the concentration of excited atoms, when there are no impacts of the second kind, varies as we go along the axis of the absorption cell from the incident face toward the origin. Let

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[9] Malinowski Ann. d. Physik **44**, 935 (1914); Orthmann Ann. d. Physik **78**, 601 (1925).

$$n_x = 100\frac{n_2 \text{ at } r=0,\ \tau k=0,\ x=x}{n_2 \text{ at } r=0,\ \tau k=0,\ x=-a}$$

$$=100\,\frac{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)e^{-\mu_k(a+x)}}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(2\alpha N+\mu_k)}}{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(2\alpha N+\mu_k)}}$$

Whence, evaluating the denominator,

$$n_x = 170\sum\frac{\mu_k J_1(\mu_k b)e^{-\mu_k(a+x)}}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(2\alpha N+\mu_k)} \tag{13}$$

Eq. (13) is plotted in Fig. 2, and it is seen that 80 percent of the excited atoms lie in a region 1 cm from the incident face.

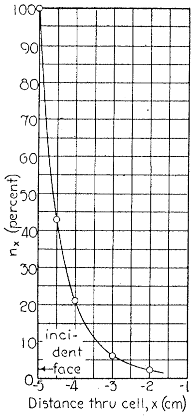

Fig. 2.

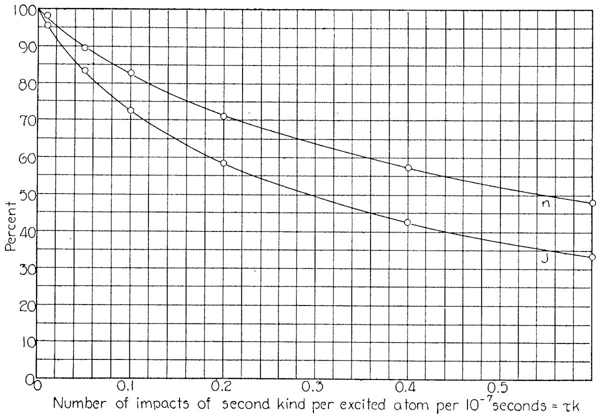

Fig. 3.

How much the number of excited atoms per cc at the incident face is reduced by impacts of the second kind can be calculated from Eqs. (11) and (12).

Let

$$n = 100\,\frac{n_2 \text{ at } x=-a,\ r=0, \text{ with impacts of second kind}}{n_2 \text{ at } x=-a, r=0, \text{ without impacts of second kind}}$$

$$=\frac{100}{1+\tau k}\,\frac{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(p_k+2\alpha N)}}{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(\mu_k+2\alpha N)}}$$

which reduces, upon evaluating the denominator, to

$$n=\frac{170}{1+\tau k}\sum\frac{\mu_k J_1(\mu_k b)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(p_k+2\alpha N)} \tag{14}$$

Values of n corresponding to values of τk equal to 0.01, 0.05, 0.1, 0.2, 0.4, and 0.6 are given in Table I, and n is plotted against τk in Fig. 3.

TABLE I. *Values of n and J for different values of τk.*

τk	n from Eq. (14)	J from Eq. (15)
0.01	98.4	95.5
0.05	89.7	83.2
0.10	82.7	72.6
0.20	71.4	58.6
0.40	57.3	42.7
0.60	48.2	33.5

From equations (3), (11) and (12), it is found that at $x=-a$, $r=0$, with impacts of the second kind,

$$I_x'=\frac{2bI_0}{c^2}\sum\frac{\mu_k J_1(\mu_k b)(2\alpha N/p_k-p_k/2\alpha N)\sinh 2ap_k}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2[2\cosh 2ap_k+(2\alpha N/p_k+p_k/2\alpha N)\sinh 2ap_k]}$$

and at $x=-a$, $r=0$, without impacts of the second kind

$$I_x'=\frac{2bI_0}{c^2}\sum\frac{\mu_k J_1(\mu_k b)(2\alpha N/\mu_k-\mu_k/2\alpha N)\sinh 2a\mu_k}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2[2\cosh 2a\mu_k+(2\alpha N/\mu_k+\mu_k/2\alpha N)\sinh 2a\mu_k]}$$

whence J, the quenching, is

$$J=100\,\frac{I_x' \text{ at } x=-a, r=0, \text{ with impacts of second kind}}{I_x' \text{ at } x=-a, r=0, \text{ without impacts of second kind}}$$

$$=100\,\frac{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)(2\alpha N-p_k)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(2\alpha N+p_k)}}{\displaystyle\sum\frac{\mu_k J_1(\mu_k b)(2\alpha N-\mu_k)}{(4\alpha^2N^2+\mu_k^2)\,[J_0(\mu_k c)]^2(2\alpha N+\mu_k)}}$$

At this point it should be emphasized that both I_x' with impacts and I_x' without impacts represent the *total* energy of radiation emitted backward per second from unit area of the incident face of the absorption cell, whereas Stuart measured the radiation included in the solid angle subtended by a lens some distance away. The final formula for J therefore is correct only if the same fraction of the total radiation passes through the lens when there are impacts, as when there are no impacts. This is undoubtedly so, since the Hg vapor pressure remained constant throughout Stuart's experiments.

Upon evaluating the denominator,

$$J = 41 \sum \frac{\mu_k J_1(\mu_k b)(2\alpha N - p_k)}{(4\alpha^2 N^2 + \mu_k^2)\left[J_0(\mu_k c)\right]^2 (2\alpha N + p_k)} \tag{15}$$

values of J for $\tau k = 0.01$, 0.05, 0.1, 0.2, 0.4, 0.6, are given in Table I, and J is plotted against τk in Fig. 3.

The curves in Fig. 3 enable us to obtain τk and n for any experimentally determined value of J. Since Stuart measured J at different pressures for many different foreign gases, we therefore have τk and n for all the foreign gases at all the pressures employed by Stuart. The first interesting piece of information is obtained by plotting τk against p. This is done in Fig. 4, and it is seen that the curves are not all straight lines. Some are linear in portions, and others are nowhere linear. The assumption usually made, that the number of impacts of the second kind per sec. per excited atom is a constant fraction of the total number of collisions, is not substantiated by these results. Consequently, we cannot ascribe to a certain gas a constant quenching efficiency.

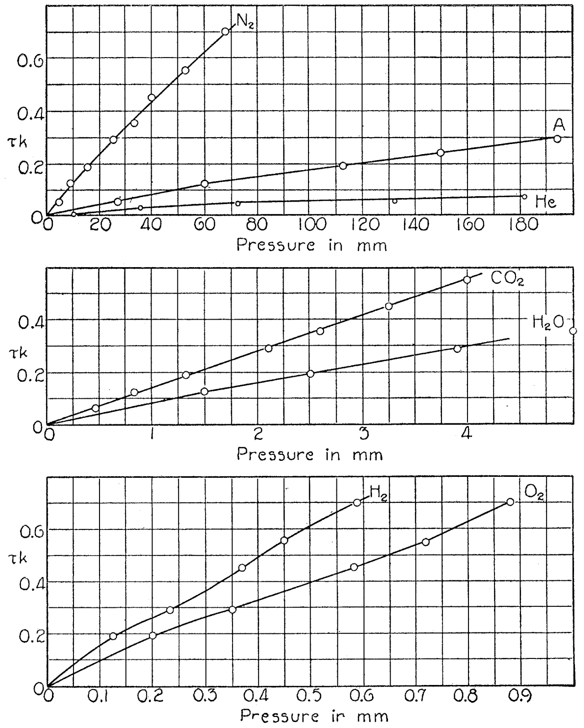

Fig. 4.

Instead, let us look at the matter from a different point of view. From the work of Franck and Cario,[4] it is shown that impacts of the second kind between excited Hg atoms and hydrogen molecules result in the dissociation of the hydrogen molecules. Similar experiments by Taylor and Marshall,[10] Taylor and Bates,[11] Mitchell,[12] Dickinson and Mitchell,[13] and Dickinson and Sherrill,[14] show that excited Hg atoms dissociate many other foreign gases, and perform other chemical reactions as well. Now, since τkn represents the number of times in 10^{-7} secs. that the excited Hg atoms in one cc at the incident face give up their energy to foreign gas molecules, and since most of the excited Hg atoms exist at the incident face, τkn can be taken as a convenient measure of the average reaction velocity. For example, τkn for hydrogen, CO_2, and H_2O represents the rate of dissociation, for O_2 either the rate at which HgO or O_3 is forming or the rate at which O_2 is being dissociated (if this takes place at all), and for N_2, A and He, the rate, possibly of activation, or complex molecule formation, etc. In other words, τkn represents the rate of change of condition of the foreign gas,—therefore the reaction velocity, and curves obtained from plotting τkn against p for all the foreign gases will show how the reaction velocity depends upon the pressure. In Fig. 5, log τkn is plotted against log p and the regularity is apparent. They are all straight lines with slopes varying from 0.54 to 0.66, the average being 0.60. Consequently we have the result that the reaction velocity near the incident face (the only place where any appreciable effect exists) is proportional to the 0.6 power of the pressure, for all the foreign gases.

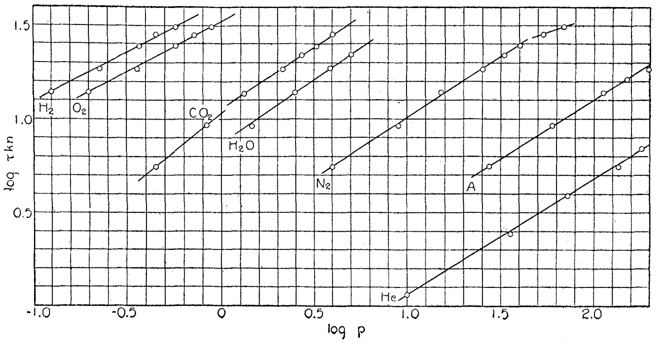

Fig. 5.

Discussion

The result just obtained, that the reaction velocity varies as a fractional power of the pressure, suggests that the quenching ability of a foreign gas is evidence of a heterogeneous gas reaction. The only gas reactions of frac-

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[10] Taylor and Marshall, Journ. of Phys. Chem. **29,** 1140 (1925).

[11] Taylor and Bates, Proc. Nat. Acad. Sci. **12,** 714 (1926).

[12] Mitchell, Proc. Nat. Acad. Sci. **11,** 458 (1925).

[13] Dickinson and Mitchell, Proc. Nat. Acad. Sci. **12,** 692 (1926).

[14] Dickinson and Sherrill, Proc. Nat. Acad. Sci. **12,** 175 (1926).

tional order that are known are catalytic reactions,[15] and, as a rule, the order is determined by the adsorbing abilityof the catalyst, which, in turn, depends upon the degree to which the catalyst is saturated with adsorbed molecules. The experiments of Wood[16] which show the presence of metastable mercury atoms in a mixture of excited mercury atoms and foreign gas molecules, and the theoretical considerations which require for some of the reactions the presence of a third body, suggest that the catalyst in this case is the incident wall on which are adsorbed metastable mercury atoms. The metastable mercury atoms formed by impacts between excited mercury atoms and foreign gas molecules are known to have a long life, and it was shown by Orthmann and Pringsheim[17] that a metastable mercury atom can travel about ten thousand free paths before it gives up its energy. Therefore, in Stuart's experiments, many of the metastable Hg atoms have time to reach a wall of the absorption cell before they are destroyed, and since the greatest number of excited Hg atoms exists near the incident face, metastable Hg atoms will be arriving at the incident face in large numbers.

If we assume that these metastable Hg atoms meet adsorbed foreign gas molecules at the incident wall, and that the energy of the metastable Hg atoms (4.68 volts) added to the total heat of adsorption is sufficient to activate the foreign gas molecules, then we are in a position to account not only for the energy needed to perform the dissociations and reactions which have been observed, but also for the result that the reaction velocity varies as a fractional power of the pressure.

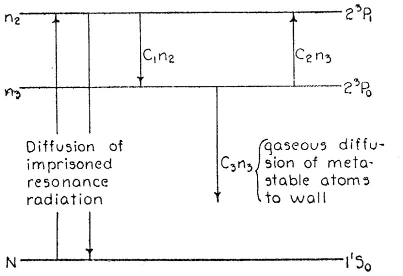

Fig. 6.

In order to derive this relation between reaction velocity and pressure, let us consider a cubic centimeter of mercury vapor near the incident wall, containing N normal Hg atoms, n_2 excited Hg atoms, n_3 metastable atoms, and a pressure p of some foreign gas. Let the rate of formation of metastable atoms be given by C_1n_2, the rate of formation of excited atoms from metastable atoms by C_2n_3, and finally the rate of diffusion of metastable atoms to the wall by C_3n_3. This scheme is shown in Fig. 6.

For equilibrium of the metastable state, we have

$$C_2n_3+C_3n_3=C_1n_2\ ;\ n_3=C_1n_2/(C_2+C_3)$$

whence

$$C_1n_2-C_2n_3=[C_1-C_1C_2/(C_2+C_3)]n_2=kn_2$$

where k has the same meaning that it had in the beginning, that is, the total number of impacts of the second kind per sec. per excited atom. Since

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[15] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926.

[16] R. W. Wood, Phil. Mag. **50**, 774 (1925).

[17] Orthmann and Pringsheim, Zeits. f. Physik **35**, 626 (1926).

$C_1n_2 - C_2n_3 = C_3n_3$, then $kn_2 = C_3n_3$, or, the reaction velocity is equal to the rate of diffusion of metastable atoms to the wall. Now, at equilibrium, the rate of arrival of metastable atoms at the wall equals the rate at which foreign gas molecules are activated at the wall, and this depends upon the degree to which the wall is saturated with metastable atoms, and the amount of foreign gas molecules adsorbed on the wall. With the wall unsaturated, the amount of foreign gas molecules adsorbed depends upon a power of the pressure,[18] and hence, the reaction velocity depends upon a power of the pressure.

If by some other agency, such as the presence of large amounts of nitrogen or argon, so many metastable atoms are produced that the wall is saturated, then the amount of hydrogen or oxygen adsorbed on the wall is independent of the pressure of the hydrogen or oxygen, and we should expect a reaction of the zero order, that is, one whose velocity is independent of the pressure. This is what was found by Meyer[19] and by Mitchell.[12] Meyer illuminated a mixture of Hg vapor, hydrogen at a pressure of 0.12 mm, and N_2 at a pressure of 7 mm, with 2537, and noticed a decrease in hydrogen pressure that was a linear function of the pressure, or $dp/dt = \text{const.}$, showing that the nitrogen provided so many metastable atoms that the amount of H_2 adsorbed by the wall was independent of the hydrogen pressure. Similarly, Mitchell used a mixture of O_2 and A and found a reaction of the zero order.

Since there is no direct evidence of the effect of the walls on gas reactions taking place in the presence of excited Hg atoms, it is not worthwhile to go any further with the ideas suggested in this paper until experiments are performed to test this point. Such experiments are in progress at the present time.

In conslusion, I should like to express my gratitude to Professor H. W. Webb for the opportunity of having many profitable discussions with him on this subject.

Physics Laboratories,
Columbia University.
February, 1928.

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[18] Tolman "Statistical Mechanics" p. 256, Chem. Cat. Co. 1927.

[19] Meyer, Zeits. f. Physik **37**, 639 (1926).