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NEW EXPERIMENTAL DETERMINATION OF EFFECTIVE CROSS-SECTIONS FOR THE QUENCHING OF MERCURY RESONANCE RADIATION

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Abstract

Theory of the quenching of resonance radiation. The problem of the quenching of resonance radiation by foreign gases is treated on the basis of Milne's theory of diffusion of radiation extended to take account of (1) a collimated incident beam, (2) a finite emission line, (3) a finite absorption line, (4) impacts of the second kind, and a curve is obtained from which one can find the number of impacts of the second kind corresponding to any experimentally observed value of the quenching. The effect of metastable atoms is discussed and a theory of their behavior outlined.

Measurement of the quenching of mercury resonance radiation. The scattered radiation emerging from an absorption cell containing mercury vapor in the presence of a foreign gas was measured as a function of the gas pressure with apparatus designed to agree closely with the requirements of the theory. From the theoretical curve the number of impacts of the second kind was obtained, and from this the effective cross-section for quenching was calculated for the following gases: O_2, H_2, CO, NH_3, CO_2, H_2O, N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, He and A. The values of the effective cross-section for quenching are tabulated along with those for depolarization of resonance radiation and for collision broadening. The quenching cross-sections of CO, NH_3, CO_2, H_2O, N_2, CH_4, C_2H_6 and C_4H_{10} are shown to be connected with the difference between the energy of the transition $2^3P_1 \rightarrow 2^3P_0$ of Hg and the vibrational energy of the molecules, in qualitative agreement with the theory of Kallmann and London.

Introduction

The quenching of mercury resonance radiation has been used by many investigators as a method of studying impacts of the second kind, and has provided rough estimates of the effective cross-sections for such impacts.[1] The most extensive investigation was carried out by Stuart[2] in 1925 who obtained quenching curves for mercury resonance radiation in the presence of H_2, O_2, CO, CO_2, H_2O, Ne, A, and He, the order representing the relative quenching ability. In Stuart's paper, and in many later papers by others,[3] attempts were made to calculate from these quenching curves the effective cross-sections associated with each gas. It is unnecessary at this point to go carefully into all the faults of these calculations, because they will become apparent in what is to follow. It is sufficient merely to mention that the

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[1] P. Pringsheim, "Fluorescenz und Phosphorescenz" Vol. VI Struktur der Materie.

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

[3] M. W. Zemansky, Phys. Rev. **31**, 812 (1928); P, D. Foote, Phys. Rev. **30**, 288 (1927); E. Gaviola, Phys. Rev. **33**, 309 (1929); E. Gaviola, Phys. Rev. **34**, 1049 (1929).

results varied widely among themselves, to such an extent that it was apparent that what was needed was not more theories to explain Stuart's curves, but new experiments performed in such a manner that they would lend themselves to accurate calculation on the basis of the existing theory of the process, namely, Milne's theory of the diffusion of radiation.

It is the purpose of this paper to treat the problem on the basis of this theory taking into account (1) the geometrical character of the incident radiation, (2) the finite spectral width of the incident radiation, (3) the geometry of the slab of mercury vapor, (4) the finite width of the absorption line, (5) the accurate value of the absorption coefficient of mercury vapor for the 2537 line. In part II new experimental data are given on the quenching of mercury resonance radiation, obtained with apparatus designed to comply with the requirements of the theory, and finally, effective cross-sections are obtained for the following gases: H_2, O_2, CO, NH_3, CO_2, H_2O, N_2, A, He, CH_4, C_2H_6, C_3H_8, and C_4H_{10}.

THEORY OF THE QUENCHING PROCESS

Consider a mass of gas, enclosed between the planes $x=0$ and $x=l$, exposed to isotropic radiation at the face $x=0$ whose frequency lies between ν and $\nu+d\nu$ and which is capable of raising the atoms from the normal state 1 to the excited state 2. Suppose at any moment that there are n_1 normal atoms per cc capable of absorbing this radiation and n_2 excited atoms per cc capable of emitting this radiation. Then it was shown by Milne,[4] on the basis of Einstein's radiation theory, *and without appeal to the analogy with molecular diffusion*, that n_2 at any point is given by:

$$\frac{\partial^2}{\partial x^2}\left(n_2 + \tau\frac{\partial n_2}{\partial t}\right) = 4\kappa^2\tau\frac{\partial n_2}{\partial t} \tag{1}$$

where τ is the life-time of the excited atom in sec, and κ is the absorption coefficient of the gas in cm^{-1} for the radiation between ν and $\nu+d\nu$. This equation holds for all values of n_2 and n_1 provided $n_2 \ll n_1$, which is undoubtedly the case for light intensities employed in the laboratory. It is *not* restricted in the way that the molecular diffusion equation of kinetic theory is, namely, to short mean free paths. Furthermore, Milne showed that the forward flux of radiation at any point is given by

$$\pi I_+ = \frac{\pi\sigma}{n_1}\left[\left(n_2 + \tau\frac{\partial n_2}{\partial t}\right) - \frac{1}{2\kappa}\frac{\partial}{\partial x}\left(n_2 + \tau\frac{\partial n_2}{\partial t}\right)\right] \tag{2}$$

and the backward flux, by

$$\pi I_- = \frac{\pi\sigma}{n_1}\left[\left(n_2 + \tau\frac{\partial n_2}{\partial t}\right) + \frac{1}{2\kappa}\frac{\partial}{\partial x}\left(n_2 + \tau\frac{\partial n_2}{\partial t}\right)\right] \tag{3}$$

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[4] E. A. Milne, Journ. Lon. Math. Soc. 1, Part I (1926).

where

$$\sigma = \frac{q_1}{q_2}\cdot\frac{2h\nu^3}{c^2}$$

and q_1 and q_2 are the statistical weights of the normal and the excited states respectively. It must be remembered that n_1, n_2, κ, I_+ and I_- are all functions of the frequency.

The $\partial n_2/\partial t$ that appears in these expressions represents the resultant rate of formation of excited atoms under the influence of the absorption of radiation, spontaneous emission, and stimulated emission. In order to take into account impacts of the second kind, and also a superimposed collimated beam of light of the same frequency at the face $x=0$, we have to consider two further rates: (1) rate of decay of excited atoms due to impacts of the second kind equal to kn_2, and (2) rate of formation of excited atoms due to absorption of the collimated beam incident on the face $x=0$, equal to $B_{1\to 2}n_1(K'/4\pi)e^{-kx}$ where $B_{1\to 2}$ is the Einstein coefficient defined in terms of light intensity and K' is the intensity of the collimated beam before it enters the slab of gas. In virtue of Einstein's relation

$$B_{1\to 2} = \frac{q_2}{q_1}\cdot\frac{c^2}{2h\nu^3}\cdot\frac{1}{\tau} = \frac{1}{\sigma\tau}$$

rate (2) can be put in the form $(n_1K'/4\pi\sigma\tau)\cdot e^{-\kappa x}$.

We have now to replace $\partial n_2/\partial t$ in Eqs. (1), (2), and (3) by

$$\frac{\partial M_2}{\partial t} + kn_2 - \frac{n_1K'}{4\pi\sigma t}e^{-kx}$$

and to put the new $\partial n_2/\partial t$ equal to zero, in order to represent the stationary state. Eq. (1) then becomes

$$\frac{\partial^2 n_2}{\partial x^2} = 4\kappa^2\frac{\tau k}{1+\tau k}n_2 - 3\frac{\kappa^2 n_1 K' e^{-\kappa x}}{4\pi\sigma(1+\tau k)} \tag{4}$$

and Eqs. (2) and (3) become

$$\pi I_+ = \frac{\pi\sigma}{n_1}(1+\tau k)\left(n_2 - \frac{1}{2\kappa}\frac{\partial n_2}{\partial x}\right) - \frac{3}{2}\frac{K'}{4}e^{-\kappa x} \tag{5}$$

$$\pi I_- = \frac{\pi\sigma}{n_1}(1+\tau k)\left(n_2 + \frac{1}{2\kappa}\frac{\partial n_2}{\partial x}\right) - \frac{1}{2}\frac{K'}{4}e^{-\kappa x}. \tag{6}$$

If, now, we do away entirely with the isotropic radiation and keep only the collimated beam, we have the boundary conditions that

when $x=0$, $I_+=0$
and when $x=l$, $I_-=0$.

Putting $\gamma = 2\kappa(\tau k/1+\tau k)^{1/2}$, the solution of Eq. (4) is

$$n_2 = A\cosh\gamma x + B\sinh\gamma x - 3\frac{n_1 K' e^{-\kappa x}}{4\pi\sigma(1-3\tau k)}\cdot \tag{7}$$

Introducing the auxiliary parameter $\beta = \sinh^{-1}\sqrt{\tau k}$ and noticing that $\sqrt{1+\tau k} = \cosh\beta$, $\sqrt{\tau k} = \sinh\beta$, Eqs. (5) and (6) become

$$\pi I_{+} = \frac{\pi\sigma}{n_1}\cosh\beta\left[A\cosh(\gamma x-\beta)+B\sinh(\gamma x-\beta)\right]-\frac{3K'e^{-\kappa x}}{2(1-3\tau k)} \tag{8}$$

$$\pi I_{-} = \frac{\pi\sigma}{n_1}\cosh\beta\left[A\cosh(\gamma x+\beta)+B\sinh(\gamma x+\beta\right]-\frac{K'e^{-\kappa x}}{2(1-3\tau k)}\,. \tag{9}$$

The boundary conditions require

$$A\cosh\beta - B\sinh\beta = \frac{3n_1K'\,\mathrm{sech}\beta}{2\pi\sigma(1-3\tau k)}$$

$$A\cosh(\gamma l+\beta)+B\sinh(\gamma l+\beta) = \frac{n_1K'\,\mathrm{sech}\,\beta}{2\pi\sigma(1-3\tau k)}e^{-\kappa l}$$

whence

$$A = \frac{3\sinh(\gamma l+\beta)+e^{-\kappa l}\sinh\beta}{\sinh(\gamma l+2\beta)}\cdot\frac{n_1K'\sinh\beta}{2\pi\sigma(1-3\tau k)}$$

$$B = \frac{-3\cosh(\gamma l+\beta)+e^{-\kappa l}\cosh\beta}{\sinh(\gamma l+2\beta)}\cdot\frac{n_1K'\,\mathrm{sech}\,\beta}{2\pi\sigma(1-3\tau k)}$$

and we have, from Eq. (8),

$$\pi I_{+} = \frac{K'}{2(1-3\tau k)}\left\{\frac{3\sinh\left[\gamma(l-x)+2\beta\right]+e^{-\kappa l}\sinh\gamma x}{\sinh(\gamma l+2\beta)}-3e^{-\kappa x}\right\}$$

The scattered radiation emerging from unit area of the face $x=l$, will then be equal to:

$$\underset{x=l}{\pi I_{+}} = \frac{K'}{2(1-3\tau k)}\left\{\frac{3\sinh 2\beta+e^{-\kappa l}\sinh\gamma l}{\sinh(\gamma l+2\beta)}-3e^{-\kappa l}\right\}$$

and finally, putting in the value of β

$$\underset{x=l}{\pi I_{+}} = \frac{K'}{2(1-3\tau k)}\left\{\frac{6(\tau k(1+\tau k))^{1/2}+e^{-\kappa l}\sinh 2\kappa l\left(\frac{\tau k}{1+\tau k}\right)^{1/2}}{\sinh\left(2\kappa l\left(\frac{\tau k}{1+\tau k}\right)^{1/2}+2\sinh^{-1}(\tau k)^{1/2}\right)}-3e^{-\kappa l}\right\} \tag{10}$$

$$= K'F(\kappa l, \tau k)\,. \tag{11}$$

Two special cases are of interest, namely $\tau k=0$ and $\tau k=1/3$. When $\tau k=0$

$$F = \frac{1}{2}\left[\frac{3-(3+\kappa l)e^{-\kappa l}}{1+\kappa l}\right]$$

and when $\tau k = 1/3$, going back to Eqs. (4), (5), and (6), we get

$$F = \frac{3}{4}\left[\frac{6\kappa l - 1 + e^{-2\kappa l}}{9e^{\kappa l} - e^{-\kappa l}}\right]$$

The function F was evaluated for a number of values of κl and of τk, and the results are given in Table I and in Fig. 1.

Table I. *Values of*

$$F(\kappa l,\ \tau k) = \frac{1}{2(1-3\tau k)}\left[\frac{6(\tau k(1+\tau k))^{1/2} + e^{-\kappa l}\sinh 2\kappa l\left(\dfrac{\tau k}{1+\tau k}\right)^{1/2}}{\sinh\left(2\kappa l\left(\dfrac{\tau k}{1+\tau k}\right)^{1/2} + 2\sinh^{-1}(\tau k)^{1/2}\right)} - 3e^{-\kappa l}\right].$$

κl \ τk	0	0.05	0.10	0.20	0.333	0.50
0.5	.194	.175	.164	.143	.125	.107
1.0	.290	.260	.236	.198	.160	.128
1.5	.332	.282	.244	.195	.150	.118
2.0	.344	.273	.227	.168	.124	.092
2.5	.334				.0968	
3.0	.320	.219	.163	.106	.0704	.0488
3.5	.300				.0504	
4.0	.280	.158	.104	.0590	.0351	.0224
4.5	.260				.0241	
5.0	.243	.108	.0628	.0308	.0163	.00968

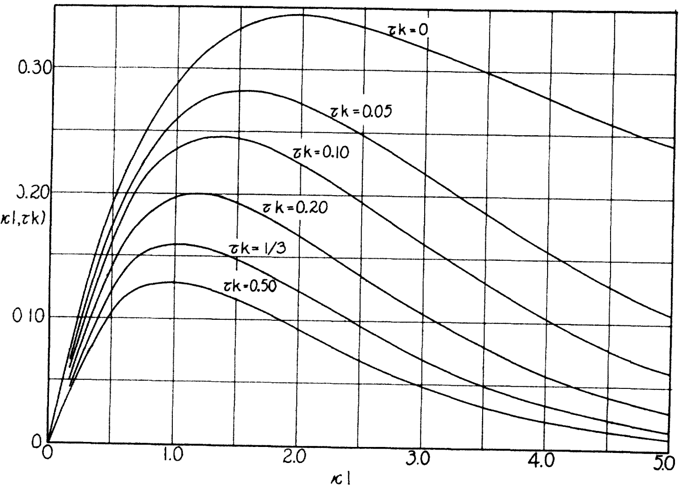

Fig. 1. The function F evaluated for a number of values of κl and of τk.

It will be remembered that this calculation was carried out for only an infinitesimal frequency band lying between ν and $\nu+d\nu$. Let us therefore write Eq. (11) as follows:

$$\pi I_{+}(\nu,\ l,\ \tau k) = K(\nu,\ 0)F(\kappa(\nu)l,\ \tau k).$$

We now assume that the emission line can be represented by a Gauss error curve of half-breadth $\Delta\nu_E$, and that the values of τk correspond to foreign gas pressures that are so small that no Lorentz collision broadening results. Then the absorption line can also be represented by a Gauss error curve whose half-breadth is the Doppler breadth, $\Delta\nu_D$. We have then

$$K(\nu, 0) = K(\nu_0, 0)e^{-[2(\nu-\nu_0)/\Delta\nu_E\cdot(\log_e 2)^{\frac{1}{2}}]2}$$

$$\kappa(\nu) = \kappa(\nu_0)e^{-[2(\nu-\nu_0)/\Delta\nu_D\cdot(\log_e 2)^{\frac{1}{2}}]2}$$

or, calling

$$\frac{2(\nu - \nu_0)}{\Delta\nu_D}(\log_e 2)^{1/2} = q$$

$$K(\nu, 0) = K(\nu_0, 0)e^{-(q\Delta\nu^{-}/T\nu_D)}$$

$$\kappa(\nu) = \kappa(\nu_0)e^{-q^2}$$

The *total* scattered radiation emerging from unit area of the face $x = l$ is

$$S = \int_0^\infty \pi I_+(\nu, l, \tau k)d\nu$$

$$= \int_0^\infty K(\nu_0, 0)e^{-(q\Delta\nu_E/\Delta\nu_D)^2}F\left[\kappa(\nu_0)le^{-q^2}, \tau k\right]d\nu$$

where the integration is to be extended over all the fine structure components of both the emission and the absorption lines.

The total incident radiation per unit area is

$$K_0 = \int_0^\infty K(\nu_0\ 0)e^{-(q\Delta\nu_D/\Delta\nu_E)^2}d\nu$$

and the "quenching" is

$$J = \frac{S/K_0 \text{ for } \tau k = \tau k}{S/K_0 \text{ for } \tau k = 0}$$

$$= \frac{\int_{-\infty}^\infty e^{-(q\Delta\nu_E/\Delta\nu_D)^2}F\left[\kappa(\nu_0)le^{-q}, \tau k\right]dq}{\int_{-\infty}^\infty e^{-(q\Delta\nu_E/\Delta\nu_D)^2}F\left[\kappa(\nu_0)le^{-q^2}, 0\right]dq} \qquad (12)$$

J can be obtained by graphical integration with the aid of Fig. 1 as soon as $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_D$ are known. A complete discussion of these quantities for mercury vapor will be found in a recent paper by the author.[5] In these experiments $\kappa(\nu_0)l$ was 4.44 and $\Delta\nu_E/\Delta\nu_D$ was 1.21. The results of the graphical integration are given in table II and Fig. 2. From Fig. 2 we can obtain τk for any experimentally determined value of J. It is seen that, when $J = 0.50$, $\tau k = 0.114$, a result very different from what would be obtained if

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[5] M. W. Zemansky, Phys. Rev. 36, 219 (1930).

the theorem of Stern and Volmer[6] were used. According to this theorem, which was used by Stuart in interpreting his quenching curves, when $J=0.50$, $\tau k=1$.

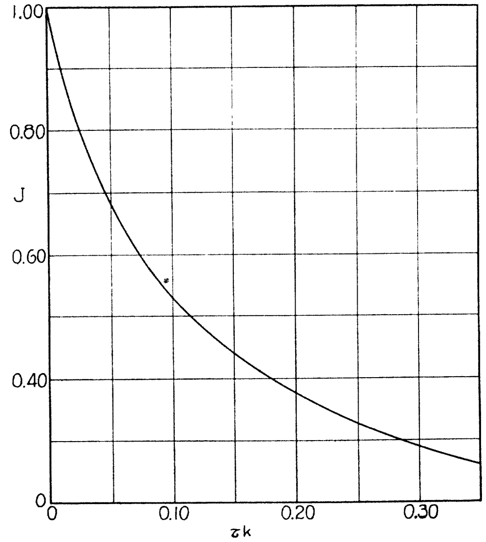

Fig. 2.

TABLE II.

$$J=\frac{\int_{-\infty}^{\infty} e^{-(q/\Delta\nu_E/\Delta\nu_D)^2}F(\kappa(\nu_0)le^{-q}\,,\,\tau k)dq}{\int_{-\infty}^{\infty} e^{-(q/\Delta\nu_E/\Delta\nu_D)^2}F(\kappa(\nu_0)le^{-q^2},\,0)dq}$$

τk	J
0.00	1.000
0.05	.683
.10	.528
.20	.374
.333	.268
.50	.199

APPARATUS AND METHOD

The essential difference between the method of Stuart and the one used here is that Stuart measured the resonance radiation that was re-emitted from the incident face of the resonance lamp that contained the foreign gas, whereas, in these experiments, the scattered radiation that passed *through* a slab of mercury vapor in the presence of a foreign gas was measured. Experimentally, Stuart's method is simpler, but it does not lend itself to accurate calculation. The apparatus used in these experiments was designed to comply with the calculation that has just been given. It is shown

[6] O. Stern and M. Volmer, Phys. Zeits. **20**, 183 (1919).

schematically in Fig. 3, and is exactly the same apparatus that was used to measure the absorption and collision broadening of the mercury resonance line. The arc, resonance lamp, and absorption cell are all described in the paper just referred to along with the manner in which the photoelectric cell was sensitized. The geometrical features of the photoelectric cell which are important in measuring the scattered radiation are shown in Fig. 4. The grid, a coarse mesh of fine platinum wire spot-welded to a circular frame of heavy platinum wire, was mounted against the window of the cell, and the plate, a cup-shaped piece of platinum, was placed as close as possible to the grid. The plate could receive, therefore, a large solid angle of radiation from a source immediately outside the window.

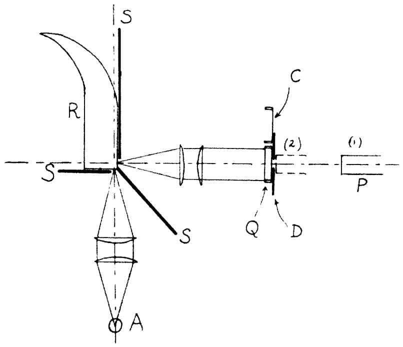

Fig. 3. Diagram of apparatus. A, arc. S, shield. R, resonance lamp. Q, absorption cell (can move to be replaced by C). C, cellophane (can move to be replaced by Q). D, diaphragm (stationary in space). P, photoelectric cell (can move from position (1) to position (2)).

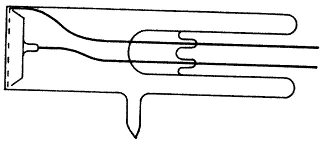

Fig. 4. Photoelectric cell.

The radiation passing through the diaphragm D in Fig. 3 is composed of two parts: the unabsorbed portion of the incident collimated beam K,[7] and the scattered resonance radiation S. When the photoelectric cell is in position (1), about 7 cm away from the diaphragm, it receives an entirely negligible fraction of S, and consequently, in this position K/K_0 can be measured in the manner described in the paper on absorption. With the photoelectric cell in position (2), close up against the diaphragm, both K and a constant fraction of S are received, say $K+\epsilon S$, and the measurement of $(K+\epsilon S)/K_0$ is made. Subtracting K/K_0 from $(K+\epsilon S)/K_0$, we get $\epsilon S/K_0$, and dividing by $\epsilon S/K_0$ when no foreign gas was present, J is obtained.

[7] $K = \int_0^\infty K(\nu,l)d\nu$, $K_0 = \int_0^\infty K(\nu,0)d\nu$ and $K' = K(\nu,0)$.

The fraction ϵ depends upon the relative size of the diaphragm and photoelectric plate, the distance between them, and the law of distribution in angle of the emerging resonance radiation. It was judged to be in the neighborhood of 90%. No attempt was made to take into account the difference between the reflecting power of the quartz window of the photoelectric cell for the collimated radiation and that for the scattered radiation, because it is believed that the error was within experimental error. The mercury vapor in the resonance lamp was kept at a density corresponding to 0°C by suitable ice baths, and the drop of mercury in the stem of the absorption cell was kept at 20°C with an allowance of no more than ±0.05°C. Under these conditions $\kappa(\nu_0)l$ and $\Delta\nu_E/\Delta\nu_D$ are known to be 4.44 and 1.21 respectively.

Every precaution possible was taken to insure purity and dryness of the gases that were studied. The pressures employed never reached a value sufficient to cause Lorentz collision broadening. It was not possible to test carefully the degree to which the absorption cell (which was 0.792 cm thick and 4.5 cm in diameter) approximated the infinite slab required by theory. No change, however, was observed in the value of J when the

TABLE III.

Gas	Pressure in mm: p	J	τk from Fig. 2
H_2	0.010	0.90	0.011
	.021	.84	.019
	.030	.74	.037
	.043	.71	.044
	.052	.68	.051
	.065	.62	.067
	.072	.59	.076
	.090	.56	.087
	.100	.49	.119
	.107	.48	.124
	.127	.43	.155
	.160	.37	.203
O_2	.033	.83	.021
	.043	.80	.026
	.056	.72	.041
	.078	.68	.051
	.078	.66	.056
	.082	.65	.058
	.112	.60	.073
	.120	.61	.070
	.120	.57	.083
	.143	.54	.095
	.150	.51	.108
	.177	.46	.136
CO	.139	.81	.024
	.22	.70	.047
	.26	.66	.056
	.27	.66	.056
	.36	.61	.070
	.45	.54	.095
	.54	.48	.127
	.59	.47	.133
NH_3	0.15	0.78	0.029
	.38	.60	.074
	.49	.56	.087
	.57	.49	.118
	.75	.45	.142
CO_2	.38	.72	.041
	.63	.62	.067
	1.02	.51	.111
	2.73	.26	.351
H_2O	1.0	.63	.064
	1.5	.54	.095
	2.33	.41	.170
N_2	1.35	.88	.014
	2.62	.80	.026
	2.95	.795	.027
	4.04	.72	.041
	5.00	.69	.048
	5.70	.65	.058
	7.50	.58	.078
	8.00	.59	.076
C_3H_8	.46	.80	.026
	1.04	.61	.070
	2.10	.43	.155

diameter of the diaphragm D was varied from 0.5 cm to 1 cm, and when the diameter of the collimated incident beam was varied slightly. It is believed that a cell whose diameter is roughly five times its thickness is a good experimental approximation to an infinite slab.

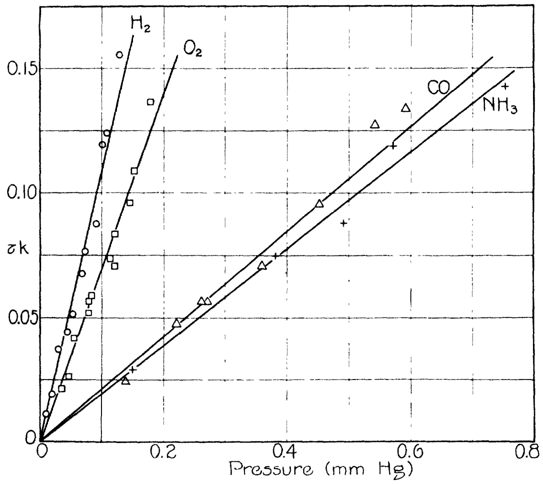

Fig. 5. τk plotted against pressure, p.

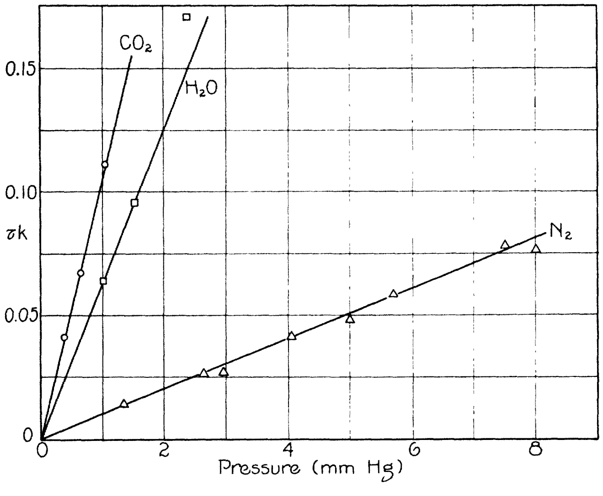

Fig. 6. τk plotted against pressure, p.

Values of J at various pressures for all the gases studied are given in Table III along with the values of τk obtained from Fig. 2, and τk is plotted against the pressure p in Figs. 5 and 6.

FINAL RESULTS

It is seen in Figs. 5 and 6 that the curves of τk against p are all straight lines. It will be remembered that k was defined as the number of impacts of the second kind per second per excited atom. By an impact of the second kind, we mean here *any* process, other than spontaneous or stimulated emission, which transfers the excited mercury atom from the 2^3P_1 state to *any* other state, not necessarily to the normal state. For example, in the case of N_2, k probably represents the number of times per sec that an excited 2^3P_1 mercury atom is lowered to the metastable 2^3P_0 level. The fact that the τk against p curve for N_2 is a straight line, indicates that the metastable atoms formed are destroyed by diffusion to the walls so rapidly that the number of upward transitions from 2^3P_0 to 2^3P_1 is negligible. If this were not so, the curve would not be a straight line. This point will be treated more fully later. If the effect of some gas is to perform both transitions, $2^3P_1 \rightarrow 2^3P_0$ and $2^3P_1 \rightarrow 1^1S_0$, then k is the sum of the rates at which each go on. Since, however, it is impossible to separate the two parts of k in this case, we shall have to be content to describe the effect of each gas as due to either one or the other of these transitions. It is not likely that a gas will perform both with equal probability. A mixture of two gases, however, should give a value of k equal to the sum of the separate values. This was tested by comparing the effect of air with the effect of N_2 and O_2. For O_2, $\tau k = 0.68p$; for N_2, $\tau k = 0.01\ p$; and for air, $\tau k = 0.14\ p$, whence for $p = 1$, $1/5 \times 0.68 + 4/5 \times 0.01 = 0.144$ in good agreement.

From kinetic theory we have,

$$\tau k = 2\tau\sigma_E{}^2 p \frac{9.71 \times 10^{18}}{T}\left(2\pi k'T\left(\frac{1}{m} + \frac{1}{M}\right)\right)^{1/2} \tag{13}$$

where p is the pressure in mm, T is the absolute temperature, k' is Boltzmann's constant, m is the mass of a mercury atom, M is the mass of a foreign gas molecule, and σ_E is the distance between centers at impact. We shall call $\sigma_E{}^2$ the "effective cross-section for quenching."

Since τ is 10^{-7} secs and $T = 293°\text{K}$

$$\frac{\tau k}{\sigma_E{}^2 p} = 3.32 \times 10^3\left(\frac{1}{m} + \frac{1}{M}\right)^{1/2} \tag{14}$$

and from Figs. 5 and 6

$$\tau k/p = \text{slope of line in Fig. 5 or 6}$$

from which $\sigma_E{}^2$ can be calculated. The values of $\tau k/p$, $\tau k/\sigma_E{}^2 p$, $\sigma_E{}^2, \sigma_N{}^2$ are given in the first four columns of Table IV. σ_N is the sum of the radius of a mercury atom (1.80×10^{-8} cm) and the gas-kinetic radius of a foreign gas molecule. The point of view adopted heretofore has been that there is associated with the excited Hg atom and with each foreign gas molecule a constant radius, and that the total number of collisions between them is given by substituting the sum of these radii for σ_E in Eq. (13). Then the number of impacts of the second kind is obtained by multiplying the right hand member of Eq. (13) by a probability. In all of the papers on this subject one will find estimates of the radius of an excited Hg atom and calculations of these probabilities. The point of view adopted here is

TABLE IV.

Gas	(1) $\tau k/p$ from Figs. 5 and 6	(2) $\tau k/\sigma_E^2 p \times 10^{-15}$ from Eq. (14)	(3) $\sigma_E^2 \times 10^{16}$ Quenching	(4) $\sigma_E^2 \times 10^{16}$ Normal	(5) $\sigma_E^2 \times 10^{16}$ depolarization	(6) $\sigma_E^2 \times 10^{16}$ collision broadening
O_2	0.683	0.491	13.9	10.7	5.70	65.1
H_2	1.10	1.83	6.01	8.89	3.55	24.5
CO	.212	.521	4.07	11.6		44.5
NH_3	.192	.653	2.94	10.8		71.2
CO_2	.107	.431	2.48	11.6	53.4	125.
H_2O	.0637	.638	1.00	10.0	51.4	68.5
N_2	.0100	.521	.192	11.2	36.4	51.0
CH_4	.004	.671	.0596	11.6		42.3
C_2H_6	.021	.506	.415	16.4		
C_3H_8	.070	.431	1.62			73.5
C_4H_{10}	.158	.385	4.11			
He	0.00	1.29	0.00	7.83	10.7	15.0
A	0.00	.448	0.00	10.4	19.0	61.5
Hg		.258		13.0	15500	

more in line with the ideas of quantum mechanics in which one is inclinde to ascribe a cross section to each *process* that can take place between two colliding molecules. Of course the two points of view amount to the same thing numerically, because the σ_E^2 in Eq. (13) is equal to

$$\text{probability} \times (\text{excited Hg radius} + \text{foreign molecule radius})^2$$

Using the values of probability and excited Hg atom radius obtained by Stuart,[2] and by Gaviola,[3] and using the low pressure parts of the $\tau k - p$ curves given in the author's previous paper on this subject,[3] the corresponing values of σ_E^2 were obtained and compared with those in Table IV. The comparison is shown in Table V.

TABLE V. *Comparison of values of effective cross-section for quenching.*

Gas	$\sigma_E^2 \times 10^{16}$ Stuart 1925	$\sigma_E^2 \times 10^{16}$ Gaviola 1929	$\sigma_E^2 \times 10^{16}$ Author 1928	$\sigma_E^2 \times 10^{16}$ These Experiments
O_2	59		20	13.9
H_2	27	20	8.8	6.01
CO	48	54	13	4.07
CO_2	12		3.2	2.48
H_2O	3.9	3.8	1.2	1.00
N_2	.63	2.0	.23	.192

The values given in Table IV for the hydrocarbons were obtained from measurements of the quenching by Bates[8] who used the same method as that employed here. In order to avoid the tedious graphical integration that is necessary to obtain the correct $J - \tau k$ curve for Bates' apparatus, the following method was used: A $\tau k - p$ curve was obtained with *this* apparatus for propane and was compared with a $J - p$ curve for propane obtained with Bates' apparatus. From these two curves a $J - \tau k$ curve was drawn that could be used for all the other gases studied by Bates.

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[8] J. R. Bates, Journ. Amer. Chem. Soc. not yet published.

The quenching of argon and helium was tested and found to be negligible in the pressure range where there is no collision broadening. At higher pressures there would presumably be a decrease in resonance radiation, but the correct value of τk could not be inferred from the $J-\tau k$ curve of Fig. 2. It would not be worth while, moreover, to compute a set of $J-\tau k$ curves corresponding to various collision breadths, because at high pressures the rate at which metastable atoms are being raised from the 2^3P_0 to the 2^3P_1 state is no longer negligible. Approximate corrections for collision broadening were made by Bates in the case of methane at high pressures, and the effect of these upward transitions was shown very definitely.

Theory of the Effect of Metastable Atoms

Suppose that the following processes are taking place: (1) transitions from 2^3P_1 to 2^3P_0, (2) diffusion of metastables to the walls, (3) transitions from 2^3P_0 to 2^3P_1, and that, at any moment there are n_1 2^3P_1 atoms, n_0 2^3P_0 atoms and n normal atoms. Let the rate at which (1) is going on be k_1n_1, and the rate of (2) be $D(\partial^2n_0/\partial x^2)$, and the rate of (3) be k_0n_0, where D is the diffusion coefficient of metastable atoms. Then, considering the equilibrium of the 2^3P_1 and the 2^3P_0 states separately, we obtain the two equations:

$$\frac{\partial^2}{\partial x^2}[n_1(1+\tau k_1)-\tau k_0n_0] = 4\kappa^2\tau[k_1n_1-k_0n_0]-\frac{3nK'}{4\pi\sigma}\kappa^2e^{-\kappa x}$$

$$D\frac{\partial^2 n_0}{\partial x^2} = -\ [k_1n_1-k_0n_0]$$

which must be solved simultaneously. They lead to the following equations:

$$\frac{\partial^2}{\partial x^2}[n_1(1+\tau k_1)+n_0(4\kappa^2\tau D-\tau k_0)] = -\frac{3nK'}{4\pi\sigma}\kappa^2e^{-\kappa x} \tag{15}$$

$$\frac{\partial^2}{\partial x^2}(k_1n_1-k_0n_0) = \frac{4\kappa^2\tau k_1+k_0/D}{1+\tau k_1}(k_1n_1-k_0n_0)-\frac{3nK'}{4\pi\sigma}\cdot\frac{k_1\kappa^2}{1+\tau k_1}e^{-\kappa x} \tag{16}$$

which can be solved very easily.

The forward and backward fluxes of radiation are:

$$\pi I_+ = \frac{\pi\sigma}{n}\left\{[n_1(1+\tau k_1)-\tau k_0n_0]-\frac{1}{2\kappa}\frac{\partial}{\partial x}[n_1(1+\tau k_1)-\tau k_0n_0]-\frac{3}{2}\frac{K'}{4}e^{-\kappa x}\right.$$

$$\pi I_- = \frac{\pi\sigma}{n}\left\{[n_1(1+\tau k_1)-\tau k_0n_0]+\frac{1}{2\kappa}\frac{\partial}{\partial x}[n_1(1+\tau k_1)-\tau k_0n_0]-\frac{1}{2}\frac{K'}{4}e^{-\kappa x}.\right.$$

The four arbitrary constants in the solutions of Eqs. (15) and (16) are obtained from the boundary conditions that

$$\text{when } x=0\begin{cases} I_+=0 \\ n_0=0\end{cases}$$

$$\text{and when } x=l\begin{cases} I_-=0 \\ n_0=0\end{cases}$$

and finally πI_+ at $x=l$ can be obtained.

In the final integration over the emission and absorption lines, account would have to be taken of collision broadening. It has not seemed worth while to carry this out in view of the fact that no experiments have been done that can be handled by these equations. It is the opinion of the author, however, that no really reliable information can be obtained about the formation of metastable atoms until some such procedure is adopted. The information yielded by measuring the absorption of a line originating from the metastable level is not very exact. Measurements of the life-time of metastable Hg atoms in the presence of foreign gases,[9] however, can yield quite reliable values of k_0 and D but not of k_1.

DISCUSSION

According to the ideas of Kallmann and London[10] the effective cross-section for quenching should depend upon the nature of the two colliding molecules, the law of interaction between them, and the difference between the energy that one has to give and the energy that the other has to take. The law of interaction depends on whether the transition of the Hg atom is optically allowed or not. We should therefore expect those molecules which produce the transition $2^3P_1 \rightarrow 1^1S_0$ to behave differently from those which produce the transition $2^3P_1 \rightarrow 2^3P_0$. There is good evidence to show that O_2 and H_2 produce the first transition and that the other molecules produce the second.

It is generally conceded that excited Hg atoms dissociate H_2 molecules. Since the energy of an excited Hg atom is 4.86 volts and the dissociation energy of H_2 is 4.42 volts, the difference is 0.44 volts. To calculate the energy difference in the case of oxygen we have to consider two possibilities: (1) $Hg^* + O_2 \rightarrow Hg + O_2^*$, in which the oxygen molecule is raised to a vibrational level. According to Mitchell,[11] the oxygen molecule has a vibrational level exactly at 4.86 volts, making the energy difference zero. (2) $Hg^* + O_2 \rightarrow Hg + O$, which[12] required an amount of energy equal to the heat of dissociation of O_2 (5.5 volts) minus the heat of dissociation of Hg O. Estimating this last quantity from thermochemical data to be about 0.5 volt, we get for the desired energy difference, $5.5 - .5 - 4.86 = 0.14$ volts. It has not been decided which one of these processes is responsible for the quenching, but since both involve a smaller energy difference than in the case of H_2 the fact that σ_E^2 is larger for O_2 than for H_2 is at least accounted for.

The quenching cross-sections of the other molecules can be accounted for in terms of the difference between the energy that the Hg atom has to give up in the transition $2^3P_1 \rightarrow 2^3P_0$ (0.218 volts) and the vibrational energy that can be taken up by a colliding molecule. Since 0.218 volts corresponds to a wave-length equal to 5.66μ, it is necessary to find out from the infrared absorption spectrum of a gas the wave-length of that band which lies nearest

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[9] M. W. Zemansky, Phys. Rev. **34**, 213 (1929).

[10] Kallmann and London, Zeits. f. Phys. Chem. B**2**, 207 (1929).

[11] A. C. G. Mitchell, Journ. Frank. Inst. **206**, 817 (1928).

[12] A. Leipunsky and A. Sagulin, Zeits. f. Phys. Chem. B**1**, 362 (1928).

5.66μ. This information was obtained from Schaefer and Matossi's "Das Ultrarote Spektrum" for every molecule except C_3H_8 and N_2. The energy of the first vibrational state of the N_2 molecule was obtained from the International Critical Tables. The results are shown in Table VI and in Fig. 7.

TABLE VI.

Gas	$\sigma_E{}^2 \times 10^{16}$ for Quenching	Wave-length in μ of Band nearest 5.66μ	Corresponding volts $= 1.234/\lambda(\mu)$	Energy difference (volts)
CO	4.07	4.66	.265	+0.047
NH_3	2.94	6.132	.202	−0.016
CO_2	2.48	4.88	.253	+0.035
H_2O	1.00	6.267	.197	−0.021
N_2	.192		.288	+0.070
CH_4	.0596	7.67	.161	−0.057
C_2H_6	.415	6.85	.180	−0.038
C_4H_{10}	4.11	5·67	.218	0.00

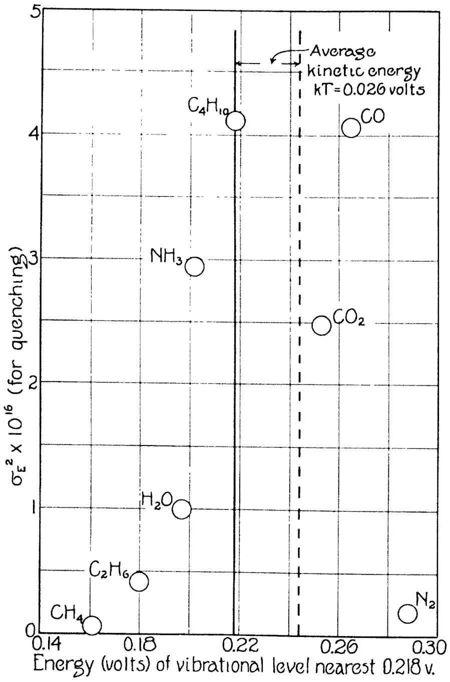

Fig. 7.

The interesting features of Fig. 7 are:

(1) The points determine roughly a "resonance curve."

(2) The points are *not* distributed symmetrically about the line drawn at 0.218 volts.

(3) The point for CO is quite far away from any curve that the other points would suggest. This discrepancy is beyond the limits of experimental error.

(4) The points are approximately symmetrical about a line drawn midway between 0.218 volts and 0.218 + average kinetic energy.

(5) There is no marked difference between the behavior of those molecules which have strong dipole moments, and those which have none. According to Kallmann and London's theory, the points should be symmetrical, and the magnitude of the cross-sections should be much larger than the normal cross-sections. One is not justified, however, in attempting to apply their theory completely to these results, because their calculation referred to a much simpler situation than the one involved here.

In columns (5) and (6) of Table IV the effective cross-sections for depolarization of resonance radiation and for collision broadening of the absorption line are given for convience in comparison. Those for collision broadening were taken from the author's recent paper,[5] and those for depolarization were calculated in the following way from data given by Keussler:[13] The percentage polarization of resonance radiation was assumed to follow the law:

$$P = \frac{P_0}{1 + \tau Z}$$

when P = percent polarization with no foreign gas, and τZ = number of depolarizing collisions per life-time per excited atom. τZ is therefore $P_0/P - 1$, and from curves of P against the pressure τZ was calculated and plotted against the pressure. The slopes of the best straight lines that could be drawn were then used to furnish values of $\sigma_E{}^2$ in the manner already described. To obtain the value for pure mercury vapor, the slope as $p \rightarrow 0$ was used, in order to eliminate the effect that the imprisonment of resonance radiation has on the depolarization.

So far, it has not been possible to find a relation between the various kinds of cross-sections, although one would expect that some relation ought to exist. In a rough way, those gases which quench most depolarize least, a result that Keussler pointed out in comparing his results with those of Stuart.

In conclusion, the author would like to thank Mr. Buttolph of the General Electric Vapor Lamp Company for the loan of a mercury arc, and Dr. J. R. Bates for his kindness in supplying data on the hydrocarbons. It is a pleasure also to express my indebtedness to Professor H. P. Robertson for very valuable help in the calculation, to Professor K. T. Compton for the privilege of working at Palmer Physical Laboratory and to the National Research Council for the opportunity to do this research.

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[13] V. Keussler, Ann. d. Physik **82,** 793 (1927).