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Effects of Temperature and Nitrogen Pressure on the Afterglow of Mercury Resonance Radiation

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Measurements have been made of the rate of decay of the λ2537 afterglow from an optically excited quartz cell containing 0.00236 mm of mercury vapor, and pressures of nitrogen ranging from 0.5 mm to 100 mm, at temperatures of 301°, 374°, and 486°K. The work was done with a rotating disk phosphoroscope so designed that two traces representing the decay of the afterglow were recorded on a photographic plate. Very pure nitrogen was necessary in order to obtain consistent results. The exponential decay constants ranged from 300 to 12,900 sec.$^{-1}$. A striking result was a very rapid increase of the decay coefficient with rise of temperature at high pressures. The rate of decay depends on the rates at which collisions with nitrogen molecules cause transitions of the mercury atom back and forth between the 2^3P_0 and 2^3P_1 states and possibly from either of these states to the normal state, on the rate of diffusion of metastable 2^3P_0 atoms to the walls of the vessel where they are reduced, and on the imprisonment of λ2537 radiation by successive absorptions and re-emissions of quanta before they escape from the cell. This latter factor depends on the frequency shape of the radiation emission and absorption coefficients and the geometry of the cell. It introduces such great mathematical difficulties into the theory that a rigorous solution for the decay constant in terms of conditions and atomic properties is not attempted here, but an approximate solution is given which, it is believed, considers all the important processes, is in excellent accord with the experimental results, and renders possible their interpretation in terms of *effective cross-sections.* From this theory and data the *effective temperature cross-sections* of excited mercury atoms for collisions with nitrogen molecules which give rise to energy transitions in the mercury atom were found to be, in the sense in which they are defined in this paper, independent of temperature in the range from 300°K to 500°K, and their mean values are:
for

$$\begin{aligned} &{}^3P_0 \to {}^3P_1 && \sigma_0^2 = 6.7 \times 10^{-18}\ \text{cm}^2 \\ &{}^3P_1 \to {}^3P_0 && \sigma_1^2 = 3.1 \times 10^{-17}\ \text{cm}^2 \\ &{}^3P_1 \to {}^1S_0 && \Sigma_1^2 \leqq 2.2 \times 10^{-18}\ \text{cm}^2 \\ &{}^3P_0 \to {}^1S_0 && \Sigma_0^2 \leqq 2.0 \times 10^{-22}\ \text{cm}^2 \text{ roughly.} \end{aligned}$$

The diffusion cross section for metastable atoms increases very slowly with temperature. The values found are 15.5×10^{-16}, 17.7×10^{-16}, and 18.4×10^{-16} cm^2 respectively at 301°, 374° and 486°K.

I. INTRODUCTION

EXPERIMENTS of R. W. Wood[1] on the fluorescence and absorption in a mercury resonance lamp excited by a mercury arc with and without other gases in the lamp showed distinctly that ${}^3P_0$ metastable mercury atoms were produced in large numbers when nitrogen was introduced at a few millimeters pressure. Stuart's[2] measurements of the quenching of fluorescence resonance radiation by foreign gases, including nitrogen, indicated that the number of ${}^3P_1$ atoms was reduced by collisions of the second kind with the

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[1] Wood, Phil. Mag. **50**, 774 (1925); Phil. Mag. **4**, 446 (1927).

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

foreign gas molecules. Asada, Ladenburg and Tietze,[3] and Asada[4] showed by a fluorescence and phosphoroscopic method that $^3P_0$ metastable atoms remain in the resonance lamp when nitrogen is present for almost one hundredth of a second. Zemansky,[5] in mercury vapor alone, by a phosphoroscopic method, measured the rate at which the re-emission of $\lambda 2537$ died down after the exciting light was cut off, found that its decay rate was exponential, and too slow to be accounted for by imprisonment of the radiation by absorptions and re-emissions. He measured the decay constant as a function of mercury vapor pressure. He later[6] explained the curves by assuming that the long lifed $^3P_0$ metastable atoms are raised to the $^3P_1$ state on collision with other atoms, and that excited atoms diffuse to the walls, and are there reduced. Experiments on the lifetimes of rare gas atoms by Dorgelo and Washington,[7] Meissner and Graffunder,[8] Eckstein,[9] and Ebbinghaus,[10] also show that diffusion to the walls and collisions with other atoms serve to reduce metastable atoms.

Dorgelo[11] observed that rise of temperature decreased the lifetimes of metastable neon and mercury atoms, and explained the effect qualitatively as due to collisions. Cario and Franck[12] measured the quenching of mercury resonance radiation by nitrogen, by hydrogen, and by mixtures of the two at 750°C and at ordinary temperatures. It was found that nitrogen did not quench the radiation, that hydrogen did, and that adding nitrogen to hydrogen increased the quenching at the high temperature, while at low temperature both nitrogen and hydrogen quench and their effects are additive. These phenomena they explained very beautifully in a qualitative way on the basis of diffusion of metastable atoms to the walls, interchange between $^3P_0$ and $^3P_1$ states of mercury by collisions with nitrogen, and reduction of $^3P_0$ or $^3P_1$ atoms to the normal state by collisions with hydrogen, and rapid increase of the number of $^3P_0 \rightarrow {}^3P_1$ transitions on collision with nitrogen because many more collisions would have the required 0.218 electron-volts of relative kinetic energy at high temperatures.

An interesting early paper by Foote[13] which attempted to interpret Stuart's quenching curves, gave a clear exposition of the processes involved in such experiments, and included absorption and re-emission of the radiation, but omitted reduction of excited atoms at the walls, which is important.

The present research was undertaken with the object of determining how the collision processes for excited mercury atoms with nitrogen molecules are

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[3] Asada, Ladenburg and Tietze, Phys. Zeits. **29**, 549 (1928).
[4] Asada, Phys. Zeits. **29**, 708 (1928).
[5] Zemansky, Phys. Rev. **29**, 513 (1927).
[6] Zemansky, Phys. Rev. **34**, 213 (1929).
[7] Dorgelo and Washington, Kon. Ak. v. Wet. Amst. **35**, 1009 (1926).
[8] Meissner and Graffunder, Ann. d. Physik **84**, 1009 (1927).
[9] Eckstein, Ann. d. Physik **87**, 1003 (1928).
[10] Ebbinghaus, Ann. d. Physik **7**, 267 (1930).
[11] Dorgelo, Physica **5**, 429 (1925).
[12] Cario and Franck, Zeits. f. Physik **37**, 619 (1926).
[13] Foote, Phys. Rev. **30**, 288 (1927).

affected by temperature. The method chosen was phosphoroscopic observation of the rate of decay of the λ2537 afterglow due to $^3P_1$ atoms produced by collisions, after the cutting off of optical excitation, over a range of temperatures and nitrogen pressures.

To account for the results and interpret them quantitatively it was found necessary to evolve a more comprehensive theory than any hitherto given, of the processes influencing the rate of decay. Since the theory is complicated it is perhaps best to describe the experiments, show that the results fit the derived formula over a large range of measurements, and evaluate the empirical constants, before proceeding to discuss the theory and the interpretation of the constants in terms of atomic properties.

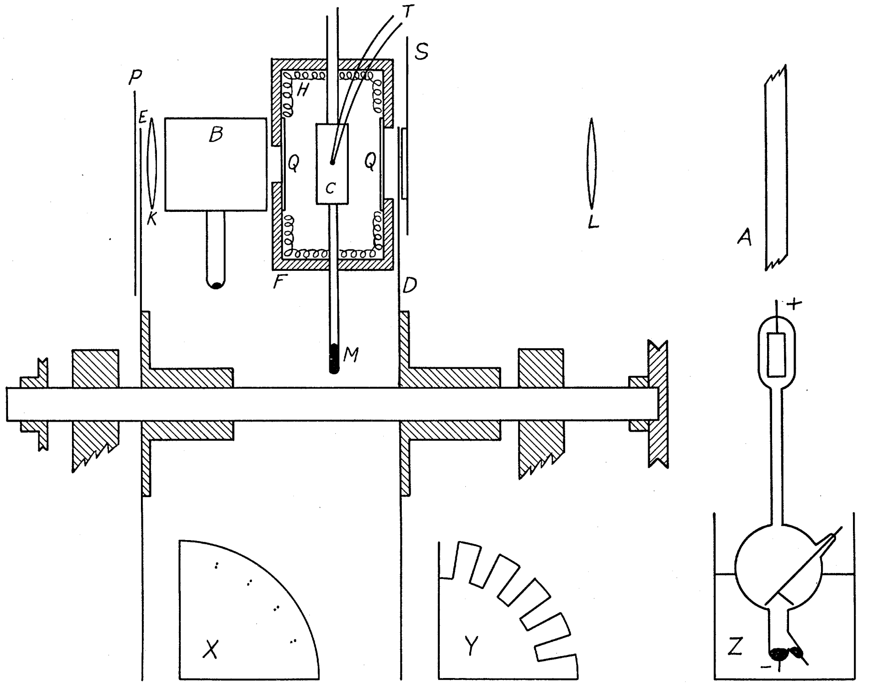

Fig. 1. The measuring apparatus. Insets: *X*—quadrant of disk *E*; *Y*—quadrant of disk *D*; *Z*—details of mercury arc *A*.

II. The Experimental Apparatus and Methods

The aim of the experiment was to measure the rate of decay of the λ2537 afterglow emitted from a quartz cell containing a small amount of mercury vapor, and several millimeters of nitrogen, after it had been excited optically for a while and the exciting light shut off. The apparatus of Fig. 1 was employed. It is essentially similar to that used by Zemansky,[5] and other workers at Columbia University.

The source of exciting light was the mercury arc at *A*, (shown in detail, at *Z*), the base of which was water cooled. The arc, once started, ran between the top and bottom electrodes at about 7 amperes, 40 volts. It was not magnetically deflected. The light was focussed by the lens L on the slit at S, which was about 2 mm wide and 3 cm long. It was then interrupted periodically by the rotating toothed wheel D, which is shown more clearly in the inset at Y. It then passed through the quartz window Q of the asbestos board furnace F, into the quartz cell C containing mercury vapor and nitrogen, where it periodically excited the mercury vapor.

Light passing through the cell or emitted by it passed out at the other window Q, through the quartz cell B which contained bromine vapor for the purpose of filtering out light due to the phosphorescence of the quartz cell C, then through the lens K which served to collimate it, and then through small holes in the rotating disk E, shown more clearly in the inset at X, onto the photographic plate at P, where it recorded a pair of traces such as shown in Fig. 2, due, during the period of the afterglow to λ2537 light only.

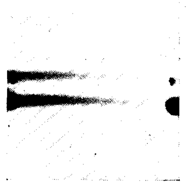

Fig. 2. Photographic traces representing the decay of λ2537.

The rotating disks were of 15 cm radius. The interrupting disk had twenty teeth 10 degrees wide, with spaces 8 degrees. The second disk had twenty 1 mm holes 18 degrees apart at 13.15 cm from the center, and twenty at 12.85 cm from the center on the same radii. The disks were set relatively to each other so that the part of the traces representing the afterglow light fell on the axial line of the cell. The cycle of excitation and afterglow was repeated twenty times per revolution of the disks. The decrease of density of the photographic trace with the angle thus represented the decrease of intensity of the afterglow with time, when the speed of the disks was known. The speed was measured with a tachometer.

Over each of the outer set of holes was cemented a piece of cellophane which transmitted 65.2 percent of λ2537 light, as determined by measurement with a photocell spectrometer apparatus. Thus the density of one trace at a given angle represented 65.2 percent of the intensity of the other trace at the same angle. A small correction was made to this for the smaller exposure time of the outer trace due to the slightly greater radius. The reciprocity law is accurate enough for such a correction. The densities of the two traces were measured and plotted as a function of angle (or time), as in Fig. 3. Since the decay of the afterglow is very nearly exponential the horizontal distance between the two traces should be constant and give the time of decay to 65.2 percent of the intensity, thus determining the decay constant β where

$$I = I_0 e^{-\beta t}$$

represents the decrease of intensity with time. This distance was not accurately constant, but was greater at the beginning than at the end. This however, is attributed to geometrical imperfections in the arrangement of the apparatus and the value at the center should be correct. The average distance was actually used to determine β and is believed to be correct within about 3 percent.

The use of cellophane to give a diminished intensity trace for calibration of the plates eliminated the intermittency errors which would occur if some of the holes were plugged according to Zemansky's procedure. The two traces are strictly comparable. It is perhaps worth while to mention that when cellophane is used for such purposes it must be pre-exposed to the light of the arc as its transmission increases several percent during the first few hours exposure, for λ2537 light, then becomes constant, at least over reasonable periods of time. (A sample of German cellophane was found to fluoresce.)

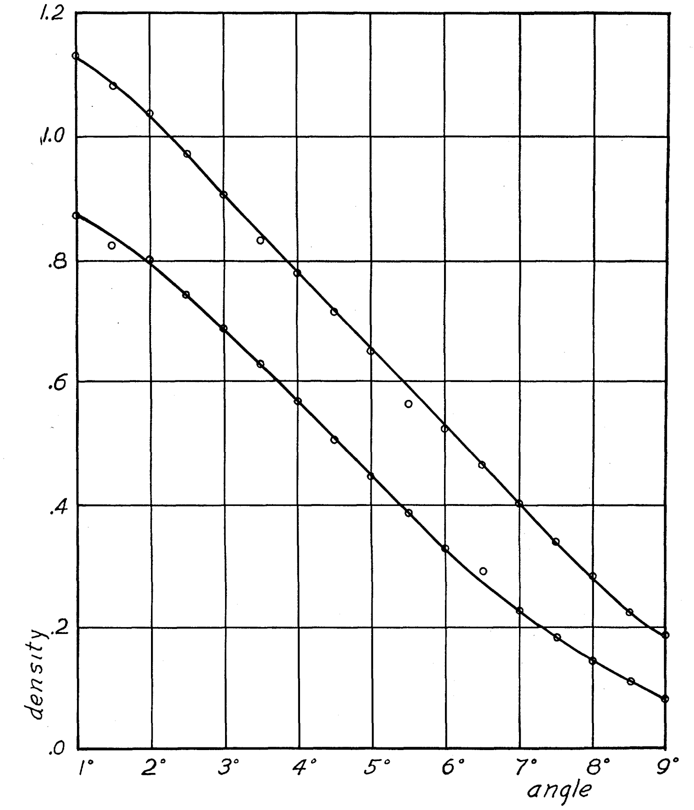

Fig. 3. The curves of density against angle for the photograph of Fig. 2. (Time is proportional to angle.)

The bromine filter in the path of the emergent light was found to be necessary to remove light due to phosphorescence of the quartz[14] of which the experimental cell was made. This phosphorescence was very intense and had

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[14] Webb and Miss Messenger, Phys. Rev. **34**, 1463 (1929).

a decay period right in the region of measurement, having a constant of roughly 3000 to 4000 sec^{-1}. Its wave-length, however, is in the blue and near ultraviolet and it was almost completely distinguished by the bromine filter which was made of quartz chosen specially because it had very little fluorescence. Tests with a spectrograph showed the filter to be entirely adequate and also showed that no light other than λ2537 was present in the afterglow after passing through the filter, so that it was legitimate to dispense with the spectrograph in making the measurements.

The furnace was heated by coils H of nichrome wire evenly distributed on its inside surface, leaving sufficient space for good circulation of air about the cell, and the temperature was measured by means of a thermocouple T, placed at the edge of the cell.

The pressure of mercury vapor inside the cell was determined by the drop of mercury in the appendix M which remained at room temperature, about 28 degrees, all the time.

Extreme purity of the gas was found to be an essential factor in obtaining consistent measurements. When impurities were present the rate of decay became very high and the intensity of the afterglow very low. This led to difficulties in the early stages of the work until their cause was ascertained and a good method of purification was adopted.

The nitrogen was prepared by the action of bromine on ammonia. Water vapor and excess ammonia were removed by allowing it to stand over phosphorus pentoxide for a considerable time. It was then admitted at a pressure of about 180 mm to a system in which it was kept in continual circulation through a mixture of copper and copper oxide at about 350°C, a trap containing glass beads at liquid air temperature, and a bulb containing phosphorus pentoxide. The gas was circulated by convection, one arm of the system being heated to about 200°C, and the process was continued for several days before the gas was used. The purification system was connected with the experimental system through a Toeppler pump equipped with a mercury seal which could be opened at will with an electromagnet. The direction of pumping was towards the purification side. When an experiment was to be performed the gas was allowed to flow very slowly through the ground surfaces of the unsealed Toeppler valve into the experimental system, and it passed through another trap with glass beads at liquid air temperature before reaching the cell C. The rate of flow was such that it took about twenty minutes to get 10 mm pressure in the cell. When all these precautions were taken it was found that consistent measurements could be obtained. The variations due to impurities were found to be much greater at high nitrogen pressures.

Before making measurements the quartz cell was thoroughly baked out so that there was no danger of gas coming off the walls of the cell. The cell was baked for an hour and a half at 450°C, and then for about the same time at 550°C, then for about 20 hours at 475°C, with the pumps on all the time. Then with the pumps shut off for $2\frac{1}{2}$ hours at the same temperature the pressure rose only to about 1 or 2×10^{-5} mm. Since the highest temperature used in the experiments was 215°C, and even before careful baking a test had shown that raising the cell to 300°C for an hour and a half between two measurements of the rate of decay at room temperature made a difference of less than 10 percent in the measurements, it was considered that this was sufficient care to ensure that no impurities arose from the cell walls during the experiment.

III. Measurements and Experimental Formulas

Measurements of the rate of decay were made as described and the exponential constants β were calculated, over a range of nitrogen pressures roughly from 0.5 mm to 100 mm, with mercury vapor at 0.00236 mm at the three temperatures 301°K, 374°K, and 486°K. The decay constants ranged from 300 to 12,900, the speed of the disks from 190 to 3660 r.p.m. The times of exposure required ranged from 2 minutes to two or three hours. It was not considered worth while to attempt to make measurements at higher temperatures because the decay constants became too large for the available speed of the disks at high pressures, and a short curve is insufficient for the evaluation of the constants in the formula.

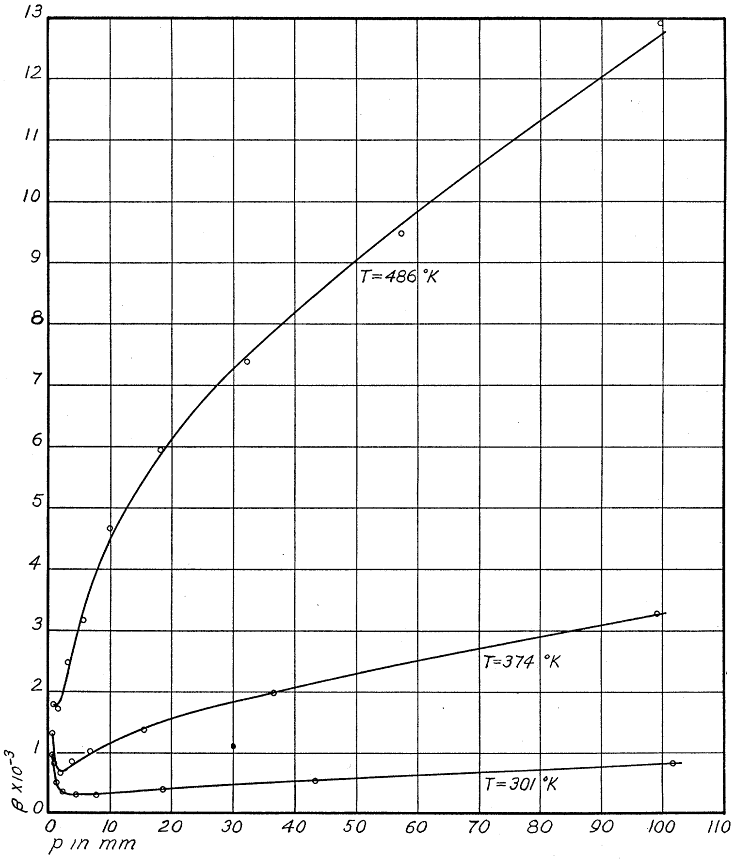

Fig. 4. Curves showing the exponential decay constant β, of the λ2537 afterglow against the pressure of the nitrogen at three temperatures.

At each temperature the procedure employed was to introduce gas very slowly into the cell until the highest pressure was reached, to make a photograph suitable for measurement, then to reduce the gas pressure to the next convenient point and make another, and proceed in this way until the pressure was the lowest convenient for making good photographs. Thus a whole set of measurements was made with the same gas, the pressure being highest for the first measurements. This procedure was adopted because it was convenient experimentally, any impurities introduced during the experiments would tend to be partially pumped out between successive pictures, and minor variations in the purity of the gas would not occur from one experiment to the next so that the curve of decay constant against pressure would be somewhat smoother and easier to fit with the formula.

Altogether about 110 photographs were taken and a great many of them measured in overcoming experimental difficulties before any of the final measurements reported in this paper were made.

The theoretical formula reduced to the form used for fitting the curves of decay constant against nitrogen pressure is

$$\beta = \frac{X}{p} + \frac{Yp + Wp^2}{p + Z} \tag{1}$$

where p is the nitrogen pressure in mm, X, Y, Z, and W are constants to be determined from the curve at each temperature, and β is the decay constant. The results are tabulated in Table I and the curves are shown in Fig. 4. The curves are plotted from the formula and the experimental points put in.

TABLE I.

p (mm)	β obs.	β calc.	% Diff.		
0.61	957	905	+5.4	$T=301$°K	
1.18	516	520	−0.8	$X=526$	
2.25	359	355	+1.0	$Y=365$	
4.4	306	306	0.0	$Z=4.7$	
7.8	301	319	−5.5	$W=4.94$	
18.6	394	393	+0.2	$E_\beta=2.6\%$	
43.3	540	535	+0.9		
101.5	832	833	−0.1		
0.57	1307	1250	+4.6	$T=374$°K	
1.02	818	847	−3.4	$X=637$	$E_X=4\%$
1.95	663	710	−6.6	$Y=1685$	$E_Y=9\%$
3.78	846	795	+6.4	$Z=6.80$	$E_Z=15\%$
6.8	1023	997	+2.6	$W=18.0$	$E_W=12\%$
15.6	1367	1409	−3.0	$E_\beta=3.80\%$	
36.6	1977	1993	−0.8		
99.2	3274	3252	+0.7		
0.87	1787	1774	+0.7	$T=486$°K	
1.57	1711	1801	−5.0	$X=909$	$E_X=7\%$
3.07	2480	2380	+4.2	$Y=7150$	$E_Y=6\%$
5.65	3160	3333	−5.2	$Z=7.75$	$E_Z=10\%$
10.0	4657	4488	+3.8	$W=65.5$	$E_W=9\%$
18.2	5935	5897	+0.6	$E_\beta=2.9\%$	
32.2	7382	7488	−1.4		
57.3	9467	9618	−1.6		
99.7	12,900	12,700	+1.6		

Several points of interest are to be noted about the shape of the curves, regarded independently of the formula. First, the rise towards a vertical asymptote at zero pressure, very marked in the two lower curves and not quite reached in the upper curve, is due to the rapid increase of diffusion of excited atoms to the walls as the pressure decreases, and indicates quite clearly that they are there removed permanently from the excited states. Second, the minimum of each curve and then the rise with increasing pressure, shows that the diffusion decreases in importance and collision processes become the dominating influence by either removing the excited atoms to some permanent state or to a state where they can radiate their energy. Third, the fact that the curves are decidedly concave downward at medium pressures and appear to be approaching an asymptote with an upward slope is an important point. If there were only interchange between the 2^3P_0 and the 2^3P_1 states to consider besides radiation, the result at high pressure would be a constant ratio of the numbers of atoms in the two states due to the rapidity of the interchange, and consequently a constant decay coefficient, and the curves would be concave downward as they rose with pressure towards this constant value. The final upward asymptote must be attributed to some process of collision which hastens the decay rate with rise of pressure for all pressures, and hence must be of the nature of removal to the normal state on collision, or else some more abstruse effect. It will be seen in the theory that it may be due partly to collision broadening of the $\lambda 2537$ line. Finally the great increase of β with temperature at high pressures is very striking. It indicates a rapid increase with pressure of some collision process. Since the metastable 2^3P_0 atoms are the only ones which have a long natural lifetime they control the slowness of the decay in order of magnitude at least and so it seems *a priori* that the process which increases so very rapidly with temperature must be removal of metastable atoms by collision. This is borne out by the theory. The curves themselves thus give a preliminary indication of the nature of the processes which must be considered in the theory.

In finding the best formulas to fit the curves a method of successive approximation was used for that at room temperature, but for the other two the least squares method was used because it was little if any more difficult and gave some information about probable errors, and the manner in which they increased with subsequent calculations based on the constants of the formulas. The probable errors of β, X, Y, Z, and W are represented in Table I by E_β, E_X, E_Y, E_Z, and E_W as they were found in the calculations. They thus represent only the magnitudes of random errors and deviations from the formula. For room temperature, since E_β is smallest, it was assumed that the magnitudes of the probable errors of the constants are about the same as for the highest temperatures.

IV. EQUATIONS FOR SOLUTION OF THE PROBLEM

The Problem.

A cylindrical cell containing a small amount of mercury vapor, and a relatively very great amount of nitrogen, is excited by light from a mercury arc for a time, and then the exciting light is stopped. We wish to express in terms of atomic properties the manner in which the intensity of the light thereafter radiated from the cell will decrease with time.

We shall throughout this paper use the terms n, 0, and 1 to denote the normal, 2^3P_0 (metastable) and 2^3P_1 states of the mercury atom, and these terms shall be used as subscripts to denote quantities pertaining to the corresponding states.

During excitation a concentration of metastable 0-atoms is built up by absorption of λ2537 and subsequent collisions of the 1-atoms with nitrogen molecules which reduce them to the 0-state. 2^3P_2 atoms may be produced during excitation by stepwise excitation, but are very rapidly removed as a result of the close resonance with a vibration level of nitrogen at 0.571 electron-volts, being reduced to $^3P_1$, so that no appreciable concentration is present at any time.[15] Their production during the decay will be very improbable because relatively few collisions have the required kinetic energy. We shall therefore neglect them.

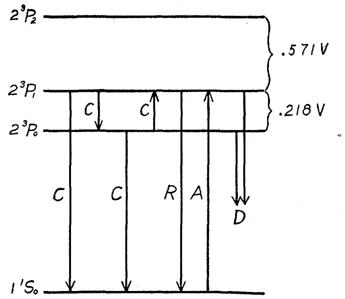

Fig. 5. Important transition processes for the mercury atom. *C*—produced by collisions; *R*—emission of λ2537; *A*—absorption of λ2537; *D*—diffusion to the walls; *V*—electron volts.

Fig. 5 indicates the types of transition which may occur by collisions with nitrogen, to radiation or absorption of λ2537, and to diffusion of excited atoms, during the afterglow period. There is interchange between the 0 and 1 states on collision, and there may be reduction of either 0- or 1-atoms to the normal state on collision. 1-atoms are reduced to the normal state by radiation of λ2537. Excited atoms lose their energy if they strike the walls of the cell and hence diffusion must be considered. This involves the geometry of the cell.

A quantum of light of λ2537 maybe absorbed and re-emitted several times before it finally escapes from the cell. The frequency distribution of the absorption line of the vapor, and the frequency distribution of the radiation density determine the number of quanta of radiation absorbed by any given element of volume. Thus consideration must be given to the diffusion of the radiation in the cell. This also involves the geometry of the cell.

All the important processes have now been enumerated, and we must proceed to express them mathematically.

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[15] Pool, Phys. Rev. **38**, 955 (1931).

The following notation will be used:

n_0, n_1, n = numbers of atoms per cc at a point in the states 0, 1, and n respectively.

N = number of nitrogen atoms per cc.

p = pressure of nitrogen in mm of mercury.

D = diffusion coefficient for 0-atoms or 1-atoms.

k_0, K_0, k_1, K_1 = numbers of effective collisions per second per mercury atom at 1 mm nitrogen pressure giving rise respectively to the transitions $0\rightarrow 1$, $0\rightarrow n$, $1\rightarrow 0$, and $1\rightarrow n$.

$\rho(\nu)d\nu$ = radiation density between the frequency ν and $\nu+d\nu$ within the λ2537 line.

$b(\nu)\,\rho(\nu)\,d\nu dt$ = probability that an n-atom will absorb a quantum in the range between ν and $\nu+d\nu$ in the time dt. This defines the coefficient $b(\nu)$.

A, B, B_{1n} = the Einstein coefficients for emission, absorption, and stimulated emission, respectively, of quanta of λ2537 radiation by mercury atoms.

g_0, g_1, g_n = statistical weights of 0-, 1-, n-states, respectively.

l = length of the cell. $l=1.65$ cm.

c = radius of the cell. $c=2.16$ cm.

We may immediately set up the equation for the rate of change of 0-atoms at a point. It is the number coming in by diffusion plus the number formed by collisions minus the number removed by collisions. Thus

$$\partial n_0/\partial t = pk_1n_1 - p(k_0+K_0)n_0 + D\nabla^2 n_0 \tag{2}$$

In finding $\partial n_1/\partial t$ radiation enters. Stimulated emission of radiation is negligible because of the Einstein relation $Bg_n = B_{1n}g_1$ and the fact that $n_1 \ll n$, whence $n_1B_{1n}\rho(\nu) \ll nB\rho(\nu)$, or the number of stimulated emissions is much smaller than the number of absorptions, whence radiation in the afterglow capable of being absorbed must be almost entirely due to spontaneous emission. Further, we may put the diffusion coefficient the same for 1- as for 0-atoms because the states are so close that there is no reason to expect any difference of behaviour for a process such as diffusion, which involves *no internal effects* on the atoms.

Thus we may write finally

$$\partial n_1/\partial t = pk_0n_0 + n\int_0^\infty b(\nu)\rho(\nu)d\nu - n_1(A + pk_1 + pK_1) + D\nabla^2 n_1. \tag{3}$$

We must solve Eqs. (2) and (3) in accordance with the boundary conditions

$$n_1 = n_0 = 0 \text{ at walls.} \tag{4}$$

So far our procedure has been rigorous, but the radiation integral in the above equation makes the problem exceedingly complicated. $b(\nu)$ depends on the five components of the line, Doppler and pressure broadening. $\rho(\nu)$ depends on $b(\nu)$ and also on the position of the point and the distribution of 1-atoms in the cell. It becomes necessary to make an approximation in dealing with the radiation terms, which gives finally a reasonably satisfactory solution.

V. The Solution

First, we shall assume that $\rho(\nu)$ is chiefly due to the radiating atoms in its immediate neighbourhood, so that it is proportional to n_1 at the same point. Then the absorption term may be represented by Ln_1, where L is an unknown coefficient which does not depend on the position of the point. Now if we put $A-L=P$ we have P representing a *resultant radiation coefficient* for the cell and each element of volume in it, and we may rewrite Eq. (3) thus,

$$\partial n_1/\partial t = pk_0n_0 - n_1(pk_1 + pK_1 + P) + D\nabla^2 n_1. \tag{5}$$

We must now solve Eqs. (2) and (5) with the boundary conditions (4). Now it is easily proved by substitution that if $\psi(x,y,z,t)$ is a solution of

$$\partial\psi/\partial t = D\nabla^2\psi \tag{6}$$

and $f_0(t)$ and $f_1(t)$ are solutions of

$$df_0/dt = pk_1f_1 - p(k_0 + K_0)\, f_0 \tag{7}$$

$$df_1/dt = pk_0f_0 - f_1(pk_1 + pK_1 + P) \tag{8}$$

then

$$n_1 = f_1(t)\psi(x,y,z,t) \tag{9}$$

$$n_0 = f_0(t)\psi(x,y,z,t) \tag{10}$$

are solutions of the complete Eqs. (2) and (5). Only the function ψ is affected by the geometrical boundary conditions (4).

Hence we may solve Eqs. (7) and (8) first. Eliminating df_0/dt and f_0 by differentiation and solving the resulting equation gives

$$f_1 = F\exp\left[-\tfrac{1}{2}\{U + (U^2-4V)^{1/2}\}t\right] + G\exp\left[-\tfrac{1}{2}\{U - (U^2-4V)^{1/2}\}t\right] \tag{11}$$

where

$$U = (pk_1 + pK_1 + pk_0 + pK_0 + P) \tag{12}$$

and

$$V = [(pk_0 + pK_0)(pk_1 + pK_1 + P) - p^2k_0k_1]. \tag{12a}$$

From the experiments of R. W. Wood[1] on absorption by 1- and 0-atoms during the steady state with illumination by λ2537 in the presence of nitrogen it is apparent that $n_1 \ll n_0$. But in that case Eq. (2) holds with $\partial n_0/\partial t = 0$, and diffusion tends to remove metastable atoms to the walls, so that

$$k_0 + K_0 \ll k_1 \tag{13}$$

Using this relation to simplify Eq. (11) we may show first that $V \ll U^2$ whence f_1 reduces first to $Ge^{-Vt/U}$ and then using Eq. (13) again, finally

$$f_1 = Ge^{-\alpha t} \tag{14}$$

where

$$\alpha = \frac{p(k_0 + K_0)P + p^2(K_0K_1 + K_0k_1 + k_0K_1)}{p(k_1 + K_1) + P}. \tag{15}$$

Similarly

$$f_0 = G'e^{-\alpha t}. \tag{16}$$

Now the solution of Eq. (6) in accordance with the boundary conditions, in cylindrical coordinates, assuming any symmetrical distribution as initial condition, gives for solution a series of terms of which only the first is of importance because the rest decay very rapidly, whence

$$\psi = G''J_0(\mu_1 r/c) \cos (\pi x/l)e^{-\gamma t} \tag{17}$$

where

$$\gamma = \left(\frac{\pi^2}{l^2} + \frac{5\cdot 81}{c^2}\right)D. \tag{18}$$

Finally by Eqs. (14), (16), (17), (9), and (10) we see that

$$n_1 = C_1 n_0 = C_2(r, x)e^{-(\alpha+\gamma)t}. \tag{19}$$

Since the radiated intensity is proportional to n_1 our experimental decay coefficient is the above exponential coefficient $\alpha+\gamma$, whence

$$\beta = \alpha + \gamma. \tag{20}$$

It is convenient at this point to introduce a small correction to the *resultant radiation coefficient* P, which is a function of the line shape. Now the line shape is affected chiefly by Doppler effect which is a function only of temperature, but it is also affected by Lorentz collision broadening, which is a function of pressure. It is desirable to reserve the term P for the result of Doppler effect and express the increase of the resultant radiation coefficient which is due to pressure broadening of the line by an added term ap, which would naturally be chosen as a first order approximation. An examination of Zemansky's[16] data on the pressure broadening effect for λ2537 with nitrogen in the same pressure range provides a rough confirmation of the view that the term ap is adequate for the purposes of this paper, that is, that it is accurate within the limits of error of the experiment. Hence we shall replace P by $P+ap$.

Then expanding our value for β, using Eqs. (15) and (18)

$$\beta = \left(\frac{\pi^2}{l^2} + \frac{5\cdot 81}{c^2}\right)\Delta + \frac{p(k_0 + K_0)P + p^2[K_0k_1 + (k_0 + K_0)(K_1 + a)]}{p(k_1 + K_1 + a) + P}. \tag{21}$$

Since $D\sim 1/N\sim 1/p$ (See Eq. (31)) we may rewrite Eq. (21) in a form suitable for application to experimental results thus:

$$\beta = \frac{X}{p} + \frac{Yp + Wp^2}{p + Z} \tag{22}$$

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[16] Zemansky, Phys. Rev. **36**, 219 (1930).

where X, Y, Z, and W are constants at a given temperature. Their values are clear by comparison with Eq. (21). The experimental results were found to agree with this formula (Section III) over a wide range of measurements.

VI. Requirements for Interpretation of Data

The first step in the interpretation is to note that by comparison of Eqs. (21) and (22)

$$k_0 + K_0 = Y/Z \tag{23}$$

$$k_1 + K_1 + a = P/Z \tag{24}$$

$$\frac{K_1 + a}{k_1 + K_1 + a} + \frac{k_1}{k_1 + K_1 + a} \cdot \frac{K_0}{k_0 + K_0} = \frac{WZ}{Y} \tag{25}$$

$$D = \frac{X}{p(\pi^2/l^2 + 5.81/c^2)} \cdot \tag{26}$$

Now Y, Z and W are known from the experimental data and are given in Table I. The value of P must be determined at each temperature by a calculation of the effect of diffusion of radiation. This calculation is a problem in itself, and the method used may have some interest apart from its application in this paper. Since it would appear in the nature of a digression here, it is carried out in Appendix B, at the end of the paper.

In order to evaluate the 'effective temperature cross sections for the various processes,' we also require the following formulas expressing k_0, K_0, k_1, and K_1 in terms of the corresponding 'cross sections' σ_0^2, Σ_0^2, σ_1^2, and Σ_1^2, for the processes involving energy transitions, and for D in terms of σ_d^2 the diffusion cross section. μ = reduced mass for mercury and nitrogen, T = temperature, k = Boltzmann's constant.

$$k_0 = \frac{2N\sigma_0^2}{p}\left(\frac{2\pi kT}{\mu}\right)^{1/2}\left(1 + \frac{\epsilon}{kT}\right)e^{-\epsilon/kT} \tag{27}$$

$$k_1 = \frac{2N\sigma_1^2}{p}\left(\frac{2\pi kT}{\mu}\right)^{1/2} \tag{28}$$

$$K_0 = \frac{2N\Sigma_0^2}{p}\left(\frac{2\pi kT}{\mu}\right)^{1/2} \tag{29}$$

$$K_1 = \frac{2N\Sigma_1^2}{p}\left(\frac{2\pi kT}{\mu}\right)^{1/2} \tag{30}$$

$$D = \frac{1}{3\pi\sigma_d^2 N}\left(\frac{8kT}{\pi\mu}\right)^{1/2} \cdot \qquad (31)^{17}$$

The factor $(1+\epsilon/kT)e^{-\epsilon/kT}$ in Eq. (27) represents the fraction of all collisions within a distance σ_0, which possesses relative kinetic energy $\geqq \epsilon$, or sufficient to produce the upward transition 0→1 in the mercury atom.

Since a discussion at this point of the definitions and nature of 'effective velocity and temperature cross sections for various processes' and derivation

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[17] Tolman, *Statistical Mechanics*, p. 228, Eq. (525) and p. 63, Eq. (95).

of formulas would again be a digression, it has been placed in Appendix A at the end of the paper.

VII. Results Independent of P

Since the calculation of P involves a further approximation, we shall first discuss those results which are independent of it.

The diffusion cross sections are calculated from the experimental values of X in Table I, by means of Eqs. (26) and (31), giving the results[17a] in Table II, under σ_d^2. They show a slow increase with temperature. Since the expected deviations would be about 6 percent this rise is probably a real one, but is slower than the square root of the absolute temperature. The sum σ of the gas-kinetic radii of the nitrogen molecule and the mercury atom results in a value $\sigma^2 = 11.2 \times 10^{-16}$ whence it appears that the cross section for metastable mercury atoms is somewhat larger than for normal atoms, as would be expected for excited atoms. This fact indicates that the assumption that all metastable atoms lose their energy at the walls is justified by the experiment. A few percent might be reflected unchanged without greatly affecting the results, but most of them are certainly reduced at the walls.

Table II.

$T°$K	σ_d^2 cm²	WZ/Y	$e^{\epsilon/kT}/(1+\epsilon/kT)$	k_0	σ_0^2 cm²
301	15.5×10^{-16}	0.0636	477	77.65	7.21×10^{-18}
374	17.7×10^{-16}	.0724	111.6	247.8	5.99×10^{-18}
486	18.4×10^{-16}	.0710	29.41	922.5	6.71×10^{-18}
	Mean Values	0.0690			6.66×10^{-18}

In order to find k_0 and σ_0^2 we must first note that by comparison of Eq. (25) with the values of WZ/Y in Table II

$$K_0 \ll k_0 \qquad K_1 + a \ll k_1 \tag{32}$$

at all three temperautres, and the maximum possible value of the ratios of K_0 to k_0 and $K_1 + a$ to k_1 is of the order of 7 percent which is within the range of possible errors of k_0 and k_1. Actually it appears later that K_0 is exceedingly small compared to k_0. We may then evaluate k_0 from Eq. (23) neglecting K_0. The values are listed in Table II.

The rapid increase of k_0 with temperature is very striking. It corresponds to a rapid rise with temperature of the number of $0 \rightarrow 1$ transitions produced by collisions, and accounts for the rapid divergence of the different (β, p) curves at high pressures as due to a rapid increase in the rate of removal of metastable atoms, in agreement with the interpretation placed on that divergence when the curves were examined.

The effective cross sections σ_0^2 may now be found from Eq. (27). The values in Table II show that within our probable random errors, which are

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[17a] Webb and Miss Messenger, since this paper was written, have published in a letter (Phys. Rev. **40**, 466, 1932) the value $\sigma_d = 3.7 \times 10^{-8}$ cm, at room temperature, which compares well with our value $3.9 = 10^{-8}$. Their experimental method and that of the author are very similar. Both are based on that of Zemansky, referred to before.

about 15 percent, σ_0^2 does not vary with temperature in the range from 300° to 500°K. It should be emphasized here that there is no *a priori* reason to expect σ_0^2 to be constant. It is shown in the appendix that an *effective temperature cross section* of this nature, from the way it is defined, must be expected to be a function of temperature. Hence our result is not merely confirmation of an *a priori* expectation, and may not hold for temperatures very different from those of the measurement.

The rapid increase of k_0 with temperature is due principally to the factor $(1+\epsilon/kT)e^{-\epsilon/kt}$ in Eq. (27) which represents the fraction of all collisions within the distance σ_0 that have sufficient relative kinetic energy ($\geqq\epsilon$) to produce the upward transition $0\rightarrow1$ in the mercury atom. This illustrates quantitatively the explanation advanced by Cario and Franck[12] for the fact that nitrogen does not quench resonance radiation at 750°C, as mentioned in our introduction.

The fact that σ_0^2 is constant implies that the corresponding *velocity cross section*, Q_0^2, must be nearly constant over the important range of velocities just above the critical relative velocity V_c corresponding to the relative kinetic energy ϵ. Since the important range of velocities is that just above the critical velocity ($\epsilon\gg kT$), the value of Q_0^2 must rise abruptly, within a few hundredths of an electron volt, from zero at the critical velocity, to its nearly constant value above it, or σ_0^2 would not appear to be independent of temperature. Thus Q_0^2 must be nearly equal to σ_0^2 in this range.

It is well to point out here that although we have referred to the nitrogen molecule as though it were a definite molecule in a definite state, the *normal state*, this is not strictly true. Actually there is a distribution of molecules among the rotational states of the lowest electronic and vibration state, due to the temperature, and principally determined by the Boltzmann factor. Since they must all be very close to the lowest state at the temperatures of our experiments, however, and it is quite impossible to differentiate between them, we have simply neglected the effect throughout.

VIII. RESULTS DEPENDING PARTIALLY ON P

Before we can evaluate k_1 and σ_1^2 we must know the values of P at the three temperatures. These values are calculated in Appendix B, to which the reader is referred, by a method involving an approximation which is consequently involved in the following calculations. The values of k_1 are obtained from Eq. (24) neglecting (K_1+a) on account of Eq. (32), using values of Z from Table I. σ_1^2 is then found by Eq. (28). The values of P, k_1 and σ_1^2 are listed in Table III.

TABLE III.

T°K	P	k_1	σ_1^2 cm²
301	0.761×10^6	1.62×10^5	3.15×10^{-17}
374	0.882×10^6	1.30×10^5	2.82×10^{-17}
486	1.058×10^6	1.36×10^5	3.37×10^{-17}
	Mean $\sigma_1^2=3.11\times10^{-17}$		

Now σ_1^2 may also have random errors of the order of 15 percent whence it is also apparently independent of temperature within the limits of error of the experiment in the range from 300° to 500°K. If we take this as correct it again implies that the velocity cross section, Q_1^2, is nearly constant and equal to σ_1^2 over the important range of velocities.

We have now found that both σ_0^2 and σ_1^2 are independent of temperature, and it is reasonable to assume that Σ_0^2 and Σ_1^2 will be essentially independent of temperature also, in order to make inferences from Eqs. (25), (29) and (30). We may then substitute in Eq. (25) from Eqs. (29) and (30), again neglecting small quantities according to Eq. (32), and get

$$\frac{a}{k_1} + \frac{\Sigma_1^2}{\sigma_1^2} + \frac{\Sigma_0^2}{\sigma_0^2}\,\frac{e^{\epsilon/kT}}{(1+\epsilon/kT)}\cdot \tag{33}$$

Now k_1 varies as $T^{1/2}$, the variation of a with temperature is unknown but probably slow so that a/k_1 varies slowly; Σ_1^2/σ_1^2 is constant, but the third term varies very rapidly due to the factor $e^{\epsilon/kT}/(1+\epsilon/kT)$. (See Table II.) Whence if Σ_0^2 has any appreciable magnitude, WZ/Y should also vary rapidly with the temperatue. Table II shows that WZ/Y is unaffected by this factor, whence we conclude that Σ_0^2 is zero within the experimental accuracy. If we attribute the 0.01 increase of WZ/Y to this term we find $\Sigma_0^2 = 2\times 10^{-22}$ as a possible order of magnitude. Hence we may say roughly

$$\Sigma_0^2 \leqq 2\times 10^{-22}\ \text{cm}^2$$

and this means that few if any metastable 2^3P_0 atoms are reduced to normal ${}^1S_0$, or otherwise permanently removed by collisions with nitrogen. This result agrees with many others which indicate that processes which take place on collision have much smaller probability for larger required change of kinetic energy.

We can now reduce Eq. (33) to

$$\frac{a}{k_1} + \frac{\Sigma_1^2}{\sigma_1^2} = \frac{WZ}{Y}\cdot \tag{34}$$

It can be shown that a/k_1 may account for an appreciable proportion (35 percent) of the magnitude of WZ/Y by a rough argument based on the data in Table IV Appendix B, and Zemansky's pressure broadening data, but its magnitude is uncertain so that from the above equation and Table II we may only assign an upper limit for Σ_1^2

$$\Sigma_1^2 \leqq 2.15\times 10^{-18}\ \text{cm}^2.$$

It does seem probable however, that Σ_1^2 has a magnitude of this order, because the value of WZ/Y is about three times the estimated collision broadening term in Eq. (34). In this case the question arises as to why Σ_1^2 should be 10,000 times greater than Σ_0^2. Several suggestions may be offered, but without undue emphasis because the subject is uncertain. There might be close resonance with the nitrogen molecules or with an impurity, so that the energy of ${}^3P_1$ could go mostly into excitation energy and require but a small change in kinetic energy, while the resonance with ${}^3P_0$ is relatively poor. Or the difference might be due to an inherent difference between optically allowed and forbidden transitions. Or it might be that a collision is capable of stimulating radiation of the allowed line λ2537. This last seems to be the most plausible way of accounting for the large ratio, particularly in view of the experiment of Cario and Franck[12] referred to before, for if Σ_1^2 has a value which does not signify production of radiation, there should be quenching at all temperatures.

IX. SUMMARY AND REMARKS

The values of the effective cross sections may now be gathered together. Those involving energy changes of the mercury atom on collision with nitrogen have all been found to be, within the limits of random error, independent of temperature in the range from 300° to 500°K. It was inferred that the corresponding velocity cross sections are nearly constant over the important range of velocities. The values of the temperature cross sections are:

$$\sigma_0^2 = 6.66 \times 10^{-18}\,\text{cm}^2, \qquad \Sigma_1^2 \leqq 2.15 \times 10^{-18}\,\text{cm}^2,$$

$$\sigma_1^2 = 3.11 \times 10^{-17}\,\text{cm}^2, \qquad \Sigma_0^2 \leqq 2.00 \times 10^{-22}\,\text{cm}^2 \text{ roughly}.$$

The first of these is the most reliable because it does not depend on the assumption used in evaluating P, the *resultant radiation coefficient.*

The diffusion cross section, σ_d^2, was found to increase slightly with temperature. The values are 15.5×10^{-16}, 17.7×10^{-16}, and $18.4\times10^{-16}\text{cm}^2$, at the temperatures 301°, 374°, and 486°K, respectively. These values are also independent of P. They are in good agreement with the assumption that metastable mercury atoms are reduced at the walls.

The theory presented in this paper and the appendix concerning the value of P appears to be quite well justified by the nature and the coherence of the results. The same kind of argument may be followed in the problem of quenching of resonance radiation, and similar approximations may be employed.

M. L. Pool[15] in a recent paper has described measurements of the rate of decay of metastable atoms of mercury in the presence of nitrogen, by a method which uses the absorption of λ4047 ($2^3P_0-2^3S_1$). He emphasizes the result that the decay is not strictly exponential but is faster at the beginning, and attributes the effect to the presence of excited metastable nitrogen atoms in the level of vibration quantum number 1 produced by previous collisions with mercury atoms in the ${}^3P_1$ state. His theory, however, neglects the important influence of the reduction of ${}^3P_1$ atoms to the normal ${}^1S_0$ or metastable ${}^3P_0$ states and imprisonment of λ2537 radiation, so that his numerical calculations of cross sections cannot be compared with those of the present paper. His measurements cover less than half the range of nitrogen pressures used in this paper, and the more rapid rise of his final exponential decay constant with pressure was the effect observed in the present investigation when traces of impurity were present. The effect of more rapid initial decay may indeed be in part due to the excited nitrogen molecules, but it should be borne in mind that some of this effect is naturally to be expected anyway in the transition from the state of affairs during excitation to the different state of affairs which holds during the decay after sufficient time has elapsed. This transition period is represented in the theory by terms of higher decay rate which have been neglected as dropping out rapidly. To justify Pool's interpretation would require a detailed examination of these terms which would be very difficult. The present experiments made no effort to detect this deviation from the exponential character, the value taken as the actual decay rate was the mean value at periods rather later than those used by Pool.

Zemansky's[18] value of the quenching cross section, 1.92×10^{-17}cm^2 for mercury resonance radiation in nitrogen, should agree with our value of $\sigma_1^2+\Sigma_1^2=(3.1+0.2)10^{-17}=3.3\times10^{-17}$, if, as he assumes, the pressure in his experiments was so low that the number of $0\rightarrow1$ transitions was negligible. The difference in these two values is apparently due to the difference in his treatment of the diffusion of radiation. Two assumptions appear implicitly in his paper. The first is that a quantum of radiation, in being absorbed and re-emitted a number of times, retains the same frequency. That this is not true may be seen by considering the Doppler effect on a quantum absorbed and then reradiated at right angles, when the absorbed and emitted frequencies are totally independent. The second assumption is that the calculations may be carried out for an element of the line and integrations with respect to frequency performed afterwards. It is impossible to estimate the error due to this procedure. However, the assumptions were made to deal with the same difficulties as those of our treatment of radiation. It does not seem possible to treat our problem by Zemansky's method, but it is possible to recalculate his quenching cross-section by methods analogous to ours. Zemansky has kindly recalculated his result for nitrogen in this way and gets the value 2.7×10^{-17}cm^2, in close agreement with our value of 3.3×10^{-17}. Since the conditions of his experiment were considerably different, such an agreement seems to provide an excellent check on the accuracy of our treatment of problem of diffusion of radiation.

The author wishes to express his sincere appreciation to Professor K. T. Compton for suggesting the subject of this investigation, to Dr. M. W. Zemansky for advice during its early stages, to Professor L. A. Turner for a great deal of helpful advice and criticism during the later parts of the work and in the preparation of this paper, and to the Department of Physics at Princeton for continued support throughout a rather prolonged research.

APPENDIX A

Collision statistics

The conception of a collision between molecules is indefinite because molecules do not have definite boundaries, but we may call a (V, q) collision one in which the relative velocity is V and the distance from the center of one molecule to the line of the relative velocity V through the center of the

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[18] Zemansky, Phys. Rev. **36**, 919 (1930).

other is q. For a (V, q) collision there is a probability $\phi(V, q)$ that a given process, say a transition of energy state, may take place, for a given pair of molecules. We know very little of the nature of the function $\phi(V, q)$. For statistical purposes however, we may define an *effective velocity cross section*, Q^2, *for the given process* by calculating the number of collisions within a distance Q at the velocity V, denote it $Z(V, Q^2)dV$ and equate it to the actual number of effective collisions at this velocity, which may be found experimentally, thereby determining Q^2. (The cross-section area is really πQ^2, but it is convenient to drop the π and refer simply to Q^2 as the cross section. This convention has been adopted with reference to all the cross sections in this paper.) Q^2 is clearly a function of velocity and of the process considered.

Since actual experiments usually do not differentiate between velocities but are carried on at a known temperature, it is convenient to make a similar definition of an *effective temperature cross-section for the given process*. If $Z(T, \sigma^2)$ represents the total number of collisions of all velocities within the distance σ at temperature T then

$$Z(T, \sigma^2) = \int_0^\infty Z(V, Q^2)dV. \tag{1}$$

We find it convenient in this paper to modify the definition slightly for the case where an amount of relative kinetic energy ϵ is required to produce the transition and equate the total number of effective collisions to the total number of collisions within a radius σ *which have sufficient relative kinetic energy* to produce the transition. Thus

$$Z(T, \epsilon, \sigma^2) = \int_{V_c}^\infty Z(V, Q^2)dV \tag{2}$$

where V_c is the critical velocity corresponding to the energy ϵ.

The σ^2 is in each case a function of temperature on account of Q^2 being a function of velocity. It is also clear from this derivation that σ^2 has no relation to the gas-kinetic radii of the atomic bodies concerned, and may be quite different for different processes. If σ^2 is known accurately as a function of temperature then Q^2 may be determined as a function of velocity through the above equations, but further information it is impossible to obtain from the results of statistical measurements alone.

To ascertain how these effective temperature cross sections depend on temperature is one of the objects of the present work. The right hand members of the above equations have occurred in our theory in the form knp, the total number of effective collisions per cc per second. The left member is easily calculated on the basis of the Maxwellian distribution[19] of velocities, and the resulting equations are Eqs. (27) to (30) of Section VI.

APPENDIX B

Diffusion of radiation and evaluation of P

In Section V of this paper the effect of diffusion of radiation was treated by the introduction of a resultant radiation coefficient, P, which was as-

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[19] Tolman, *Statistical Mechanics*, p. 69, Eqs. (121) and (122a).

sumed to be the same for every element of volume and for the cell as a whole. We wish to evaluate this coefficient. In order to do so we note that it concerns *only emission and absorption of radiation.* If our cell had no other processes occurring than these the radiation emitted would decay according to the law $I=I_0e^{-Pt}$ and P would be the exponential decay coefficient for the cell. We shall then determine P theoretically by calculating what the decay coefficient would be if only emission and absorption of λ2537 radiation occurred.

Now this problem was solved by E. A. Milne[20] for a simplified case, namely that of atomic absorption and emission coefficients which were constant over the breadth $\Delta\nu$ of the line, and an infinite plane slab of gas. His result is that the decay is dominated by the first term of a series of exponentials, and the decay coefficient of this term is (expressed in our notation),

$$P = \frac{A}{1 + (\kappa l/\lambda)^2} \tag{1}$$

where κ is the absorption coefficient, l the thickness of the slab, and λ is the root which lies between 0 and $\pi/2$ of the equation

$$\lambda \tan \lambda = \kappa l, \tag{2}$$

He interprets

$$\kappa l = C \tag{3}$$

as the *opacity* of the slab, presumably because for a collimated beam of the frequency shape assumed shining through the slab, the total transmitted intensity $I(l)$ is to the total incident intensity $I(0)$ in the ratio

$$I(l)/I(0) = e^{-\kappa l} = e^{-C}. \tag{4}$$

In an experimental case, he suggested that the opacity of the slab should be determined by measurement, and used to calculate P. This clearly is intended as a way of finding a suitable type of mean value for P, in consideration of the fact that the absorption and emission coefficients actually depend on the frequency.

In Milne's theory P is a function only of $I(l)/I(0)$, or of the fraction of incident light transmitted by the slab when the absorption and emission coefficients are independent of frequency over the breadth of the line. This fact suggests the assumption that P is a function only of the transmission (or absorbing power) of the slab even when the absorption and emission coefficients do depend on the frequency, and that the function itself is unchanged. Since we can determine the ratio $I(l)/I(0)$ we can evaluate P on the basis of this assumption, so that it is a convenient one to make for our present problem, and we shall proceed to use it. Its accuracy is perhaps open to some question, but it is hoped that it affords a good approximation. The discussion moreover, contains many ideas which are essential to any more rigorous theory. The assumption agrees with Milne's suggestion, but requires

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[20] Milne, Jour. Lon. Math. Soc. I, Part I, p. 40 (1926).

the added rather obvious statement that the light whose transmission we determine has intensity corresponding in frequency distribution to the natural radiation coefficients of the gas in the cell. We may then calculate $I(l)/I(0)$ from the known value of A, and through it obtain the value of P.

The use of a value of P derived for an infinite plane slab in the case of our cell which is cylindrical is roughly justified later, by consideration of the dimensions of the cell, in relation to the probability of a quantum escaping at the edge.

We shall calculate P for a line affected by Doppler broadening only. The effect of pressure broadening was considered before and expressed by another term, ap, so it need not be discussed here.

A consideration of the Doppler principle applied to a system of atoms moving with velocities according to the Maxwell-Boltzmann velocity distribution formula, and the definition of the half breadth of a line as the breadth $\Delta\nu$ at half the maximum height of the line, leads[21] to the formula

$$\phi(\nu)d\nu = \phi(\nu_0)e^{-4\log 2(\nu_0-\nu)^2/\Delta\nu^2}d\nu \tag{5}$$

for the probability that a quantum emitted or absorbed with proper frequency ν_0 will appear to the observer to be of frequency ν, where $\phi(\nu_0)$ is the maximum, occurring at ν_0, and

$$\Delta\nu = \left[\frac{8kI\nu_0^2}{mc^2}\log 2\right]^{1/2} \tag{6}$$

is the half breadth.

If we put

$$\omega^2 = \frac{4(\nu_0 - \nu)^2}{\Delta\nu^2}\log 2 \tag{7}$$

then the absorption coefficient

$$\kappa(\nu) = \kappa(\nu_0)e^{-\omega^2}. \tag{8}$$

Also if $I(0, \nu)$ is the intensity incident on the slab at ν, and $I(1, \nu)$ is the intensity transmitted at ν, then

$$I(0, \nu) = I(0, \nu_0)e^{-\omega^2} \tag{9}$$

in accordance with our assumption that the incident light must have the same frequency distribution as the radiation coefficients.

Then the transmitted intensity at ν is

$$I(l,\nu) = I(0, \nu)e^{-\kappa(\nu)l} = I(0, \nu_0)\exp\left[-\omega^2 - \kappa(\nu_0)le^{-\omega^2}\right]. \tag{10}$$

The total incident intensity is

$$I(0) = \int_0^\infty I(0, \nu_0)e^{-\omega^2}d\nu. \tag{11}$$

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[21] Müller-Pouillet's, *Lehrbuch der Physik*, 11 Ed. V. 2, Part 2, V. 1. Article by Minkowski discusses factors affecting shape of spectrum lines.

A similar integration of Eq. (10) gives the total transmitted intensity $I(l)$. Then, changing $d\kappa$ into terms of $d\omega$ and changing the integrations to correspond (0 becomes effectively $-\infty$), and integrating the denominator gives the required ratio

$$\frac{I(l)}{I(0)} = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} \exp\left[-\omega^2 - \kappa(\nu_0) l e^{-\omega^2}\right] d\omega. \tag{12}$$

The integral may be computed graphically when $\kappa(\nu_0)$ is known.

Now when a collimated beam $I(\nu)$ goes a distance dx the energy absorbed per cm² in $d\nu$ is $\kappa(\nu)I(\nu)d\nu dx$, but it is also $nh\nu\rho(\nu)b(\nu)d\nu dx$, and since $c\rho(\nu) = I(\nu)$ we find that

$$\kappa(\nu) = nh\nu b(\nu)/c. \tag{13}$$

From Eq. (5) it is apparent that $B\phi(\nu) = b(\nu)$, and since a quantum must appear to be absorbed at some frequency $\int_0^\infty \phi(\nu) d\nu = 1$ whence

$$\int_0^\infty b(\nu) d\nu = B. \tag{14}$$

Further, the Einstein relation[22] of radiation coefficients is

$$B = g_1 c^3 A / 8\pi g_n h \nu^3. \tag{15}$$

The value of A is known quite accurately whence, through Eqs. (13), (14), (15), (8) and (7), and assuming (as Zemansky[16] did) that the five components of the line are approximately equal, we get $\kappa(\nu_0)$ as one fifth of the value it would have if there were only a single component, namely,

$$\kappa(\nu_0) = \frac{(2 \log 2)^{1/2}}{40\pi} \frac{g_1 \lambda^2 A}{g_n} \cdot \frac{n}{\Delta\nu}. \tag{16}$$

Using the[23] value 8.75×10^6 for A

$$\kappa(\nu_0) = 1.64 \times 10^{-4} n/\Delta\nu. \tag{17}$$

The Doppler half breadth, by Eq. (6), is

$$\Delta\nu = 5.97 \times 10^7 T^{1/2} \tag{18}$$

and since the mercury vapor pressure in the experiments was that of the liquid at 28°C, namely 0.00236 mm

$$n = 2.295 \times 10^{16}/T. \tag{19}$$

Whence finally

$$\kappa(\nu_0) l = 1.04 \times 10^5 T^{-3/2}. \tag{20}$$

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[22] Ruark and Urey, *Atoms, Molecules, and Quanta*, p. 60.

[23] Ladenburg and Wolfsohn, Zeits. f. Physik **65**, 207 (1930).

Thus P may be calculated at each temperature through Eqs. (20), (12), (4), (3), (2), and (1). The course of the calculation is indicated in the following table.

TABLE IV.

T°K	$\kappa(\nu_0)l$	$I(l)/I(0)$	C	λ	P
301	19.9	0.0158	4.15	1.273	0.761×10^6
374	14.4	0.0233	3.76	1.251	0.882×10^6
486	9.7	0.0375	3.29	1.216	1.058×10^6

A rough justification of the assumption that our cell is a fairly good approximation to an infinite plane slab may be obtained from the figures of Table IV. Our method depends on the fact that the rim is relatively farther than the face of the cell so that a quantum of radiation has less chance of escaping there. Hence, we should consider the situation at the highest temperature, where the transmission is greatest, to strengthen the argument. The value of $\kappa(\nu_0)\ l$ at 1.65 cms is 9.7 whence at 2.16 cm, the radius of the cell, it would be 12.7. Now consider points on the axis of the cell. A rough interpolation gives $I(l)/I(0)=0.028$ for $\kappa(\nu_0)l=12.7$ and this is the chance of a quantum going far enough unabsorbed to escape at the rim. The solid angle is roughly $2\pi\times2.16\times1.65/2.16^2=4\pi\times0.38$. Thus the total probability of a quantum emitted at the axis of the cell escaping at the rim is $0.028\times0.38=0.0106$.

Now the probability of a quantum being emitted by a 1-atom in time dt is Adt, and the probability of a quantum escaping from an infinite plane slab is Pdt, whence the probability of an already emitted quantum escaping from the slab is $P/A=1.058\times10^6/8.85\times10^6=0.12$. Thus the added probability of escape due to the cylindrical shape of the cell, for quanta emitted close to the axis, where observations are made, is only one tenth of the total. This affords justification for the belief that the assumption is a good one, involving at least no greater error than the use of Milne's theory.

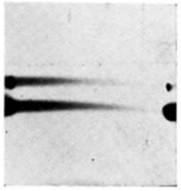

Fig. 2. Photographic traces representing the decay of λ2537.