

THE DISPERSION OF ATOMIC HYDROGEN. I—A MEASURE

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The apparatus used in the experiment which is the subject of this communication is related to that named after Puccianti.¹ It consists essentially of identical tubes about 85 cm. long with optically plane parallel ends placed in the arms of an interferometer and filled to the same pressure with hydrogen. A powerful discharge was passed through one of the tubes while "white-light" fringes from a high intensity carbon arc were being observed. The fringes were made horizontal and focussed on the narrow vertical slit of a spectroscope or a very fast spectrograph. The fiducial point was provided in the visual observations by the cross-hairs of the spectroscope and in the photographic by a very fine wire stretched horizontally across the slit of the spectrograph. The field presented was then a bright continuous spectrum traversed by a number of almost horizontal slightly curved and very black fringes and also by the very sharp horizontal shadow of the cross-hairs or the wire across the slit.

The discharge is turned on and fixing attention to a part of the spectrum not disturbed by the Balmer lines which come out in great purity,² a shift of the fringes is looked for. Otherwise a series of exposures of 1 to 4 seconds' duration is taken with the discharge alternately off and on and the position of the fringes measured with respect to the fiducial line. This procedure was repeated many times at pressures from 0 to 25 mm. with all varieties of conditions of discharge, purity of hydrogen, etc.

TABLE 1

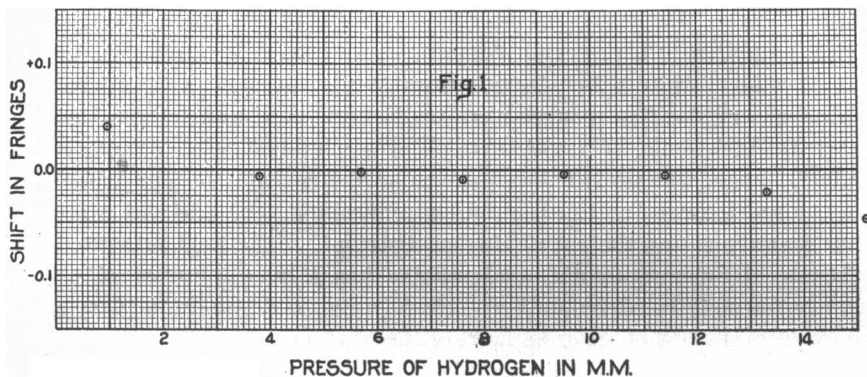
PRESSURE IN MILLIMETERS OF HG MM.	AVERAGE FRINGE SHIFT FRINGES
0.95	+0.040
1.9	-0.015
3.8	-0.006
5.7	-0.001
7.6	-0.009
9.5	-0.004
11.4	-0.005
13.3	-0.022
15.2	-0.047
19	-0.066

The shift of fringes at any wave-length together with a knowledge of the concentration of atomic hydrogen and the index of refraction of molecular hydrogen serves to determine the dispersion of atomic hydrogen.

Of course, there were precautions to take. A complete description of these, together with a discussion of the many troublesome spurious effects

encountered, is being sent to the *Physical Review* for publication. Meanwhile, the experiment is being repeated under conditions having the tremendous advantage of giving practically complete dissociation into atomic hydrogen.

Table 1 gives the average of twelve series of runs from one millimeter pressure to about two centimeters. In each series there were from 5 to 25 determinations of the shift for each pressure. Figure 1 is a graphical representation of table 1.



Each one of these individual determinations as well as every one of countless visual observations is practically the same as the average. The positive shift at the first point, the small negative deflections for intermediate pressures and the negative shift at high pressures are due to well understood disturbing influences; namely—the positive temperature coefficient of the index of refraction of the glass ends—and the negative density gradient from the axis of the tubes to the walls, respectively. Most of the readings were made at a wave-length of about $\lambda = 6000 \text{ \AA}$ but a few were taken at different places over the visible spectrum. The conclusion is that with a precision to be considered later the index of refraction of atomic hydrogen is half that of molecular hydrogen or at 1 atmosphere and 0°C . since $\mu - 1$ is small.

$$\mu_{\text{H}}^2 - 1 = \frac{1}{2} (\mu_{\text{H}_2}^2 - 1) = 1.36 \times 10^{-4}. \quad (1)$$

To find the magnitude of the possible error in this figure it is necessary to make an estimate of the partial pressure of atomic hydrogen. Unfortunately, attempts to measure this directly have hitherto been unsuccessful. There are many arguments which may be invoked to decide on a lower limit of the concentration but for the present article we shall restrict ourselves to data obtained from the splendid work of K. F. Bonhoeffer.³

In the first place attention is called to the fact that Bonhoeffer's measures of the rate of recombination of atomic hydrogen at 0.5 mm. fit exactly the law

$$\gamma = \gamma_0 e^{-kt} \quad (2)$$

where γ is the fraction of H_2 molecules dissociated and k the so-called specific rate of recombination is put equal to 2. The quantity k must be a function of the pressure which is zero when $p = 0$. Let us say for the time being $k = k_0 p^n$ and then we can write for (2)

$$\gamma = \gamma_0 e^{-2^{n+1} p^n t}, \quad (3)$$

where p is the initial pressure of molecular hydrogen in millimeters.

In our experiments the voltage was supplied from a 16,000 v. 10 kw. transformer with a large condenser in parallel and a variable spark gap in series with the tube. In a few cases the gap was closed giving a 50-cycle sine wave, at other times the gap broke down at least twice a cycle giving condensed discharges certainly less than a thousandth of a second in duration. The interval between discharges was, therefore, never more than one hundredth of a second and usually the time during which the discharge was on, was a negligible part of the cycle. The apparent position of the fringes will correspond to the average value of the dissociation which we proceed to calculate using the most unfavorable assumptions, namely, that the interval between discharges is 0.01 second. We have then

$$\bar{\gamma} = 100 \gamma_0 \int_0^{100} e^{-2^{n+1} p^n t} dt \quad (4)$$

$$= \frac{100 \gamma_0}{2^{n+1} p^n} \left[1 - e^{-\frac{2^{n+1} p^n}{100}} \right]. \quad (4')$$

The next difficulty is to decide on the pressure dependence of the initial dissociation γ_0 . Considering that in the beginning of the region of pressures used, the current through the tube for a given voltage increased with the pressure and considering the facts that at pressures up to about 1 cm., there were often several discharges per cycle and that the power and voltage inputs were increased with the pressure up to about 12 mm., it would be an underestimate at low pressures and an overestimate at high pressures to say that the initial dissociation did not decrease with increase of pressure. Since both of these are unfavorable to the conclusions we are to draw we shall make the assumption with a clear conscience. For the constant of initial dissociation we again refer to Bonhoeffer, who gives, in a very decided underestimate, 20% for the fraction γ_0 at some unmentioned pressure, probably about 0.5 mm. When the 10 kw. transformer and the short duration condensed discharges at 8000 to 16,000 v.

giving current densities of hundreds of amperes per square centimeter—while the discharge passed—(average low frequency currents over the whole cycle went up to several amperes per square centimeter) are compared with the milliamps used by Bonhoeffer, it seems conservative to write

$$\gamma_0 = 0.2$$

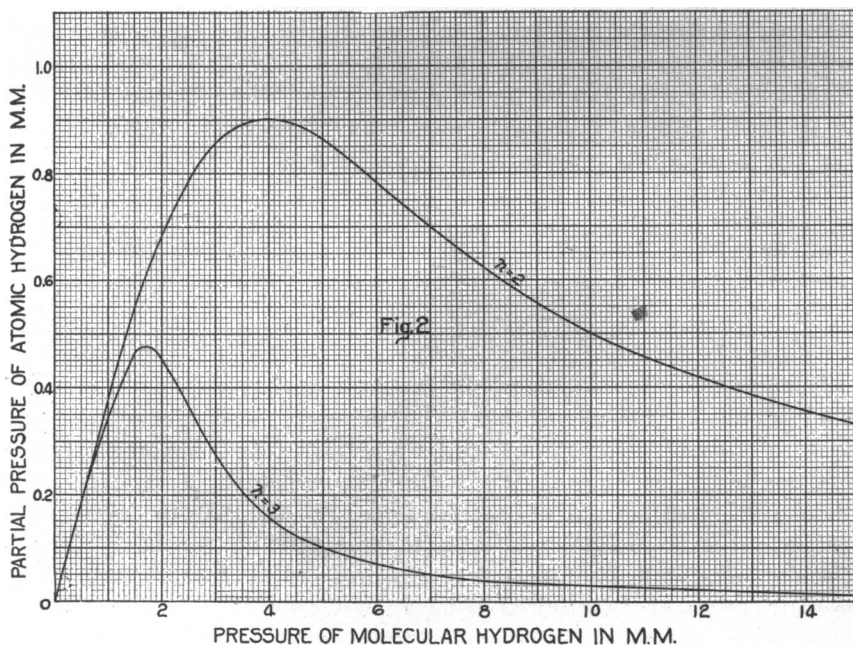
giving from (4')

$$\bar{\gamma} = \frac{10}{2^n p^n} \left[1 - e^{-\frac{2^{n+1} p^n}{100}} \right]$$

so that for the partial pressure of atomic hydrogen we have, approximately,

$$p_H = \frac{10}{2^{n-1} p_{H_2}^{n-1}} \left[1 - e^{-\frac{2^{n+1} p_{H_2}^n}{100}} \right]. \quad (5)$$

As to n , the power of the pressure according to which the rate of recombination increases it might be said that for this type of reaction $n = 2$ is plausible, but from the point of view of the chemical kinetics of Born



and Franck,⁴ it is well to consider the case $n = 3$. Figure 2 shows the partial pressures of atomic hydrogen as calculated from (5) for each of these values of n .

The maximum partial pressure of H is 0.90 mm. and 0.46 mm. for

$n = 2$ and $n = 3$, respectively. The assumptions made lead, therefore, to no extravagant values of the dissociation.

It remains to estimate how small a shift was detectable. The practised eye notices a sudden shift of $1/30$ of a fringe under favorable conditions. The measurement of a photographic plate is still better, yet we shall take it that the average values given in table 1 are reliable to 0.03 fringe. In that case, considering the disturbing influences already mentioned the fringe shift is zero for all pressures and even without allowing for these influences it is zero for the pressures where the partial pressure of atomic hydrogen is appreciable. The expression for the fringe shift ΔN caused by the formation of atomic hydrogen when the discharge is turned on may be written

$$\Delta N = K[(\mu_{H_2}^2 - 1)\Delta p_{H_2} + (\mu_H^2 - 1)\Delta p_H] \quad (6)$$

where μ_{H_2} and μ_H are the refractive indices of H_2 and H , respectively, K is a constant which calculated for case at hand is $\frac{1}{1.9(\mu_{H_2} - 1)}$ and where Δp_{H_2} and Δp_H are the changes in pressure of the two components due to the discharge. These satisfy the relation

$$\Delta p_H = -2\Delta p_{H_2}.$$

Putting $\Delta N = 0.03$ there results from (6)

$$(\mu_H^2 - 1) = [1.36 \pm 0.17] \times 10^{-4} \quad (7)$$

if $n = 2$, and

$$(\mu_H^2 - 1) = [1.36 \pm 0.34] \times 10^{-4} \quad (8)$$

if $n = 3$.

This is very crude measurement. Nevertheless, it is sufficient to discriminate against some of the dispersion formulae that have been proposed. This matter is considered in the next paper where it is shown that the formulae which are satisfactory in that they put the anomalous dispersion at the observed frequencies yield values for $(\mu_H^2 - 1)$ which differ from that given by experiment, by several times the margin indicated in (8).

It is realized that the matter cannot be regarded as settled until it is possible to take direct observations of the amount of atomic hydrogen while the dispersion is being measured. The author hopes to attempt this at the Naval Research Laboratory in Washington, D. C.

¹ L. Puccianti, *Il. Nuovo Cimento*, 2, 257 (1901). Similar arrangements have been used by D. Roschdestwensky, *Ann. Physik.*, 39, 307 (1912); R. Ladenburg and St. Loria, *Verh. D. Physik. Ges.*, 10, 858 (1908) and quite recently by R. Ladenburg, H. Kopfermann and A. Carst, *Sitz. Preuss. Akad. Wissenschaften*, 20-22, 255 (1926).

² It might be mentioned for what it is worth that under favorable conditions, with the Balmer series horribly overexposed for a width of from 50 to 200 Å. not a trace of the secondary spectrum could be seen. A few Hg and Al lines beyond the violet and a

very noticeable continuous spectrum were present. Using a moderately narrow slit, the secondary spectrum could be found visually only by those who knew just where to look for it.

³ K. F. Bonhoeffer, *Zeit. Physik. Chem.*, 113, 199 (1924).

⁴ M. Born and J. Franck, *Ann. Physik*, 76, 225 (1925) and *Zeit. Physik*, 31, 411 (1925).

THE DISPERSION OF ATOMIC HYDROGEN II—A CALCULATION

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In the preceding paper experimental evidence is brought forward to show that at a wave-length $\lambda = 6000 \text{ \AA}$ the index of refraction of atomic hydrogen is $\mu_H = 1.000068$. Expressions for this quantity derived by Sommerfeld and Epstein* check this value but cannot be taken as correct because they all require anomalous dispersion at frequencies corresponding to the mechanical frequencies of the model and nothing in particular at the spectral frequencies. It is significant that these classical computations using atomic models given by the quantum theory should give a correct result for long wave-lengths. On the other hand—as shown in this paper—attempts to adjust the dispersion formulae to give the proper frequencies for anomalous dispersion lead to a numerical value for μ_H which is decidedly too large.

The author has calculated and will publish elsewhere the perturbations of a known system by a force of the form $E_0 F(t)$. As a special case we have the problem of dispersion—namely, an atomic system acted on by a plane wave. In this case we have an electric field $E_0 \cos 2\pi\nu t$. If general cylindrical coordinates are chosen with the z direction parallel to the electric field, the expression for an element of the first order perturbation of the $2f$ dimensional matrix q_s is given by¹

$$q_s^1(n_1 \dots n_f, m_1 \dots m_f) = \frac{eE_0 \cos 2\pi\nu t}{2\pi i h m} \sum_{k_1 \dots k_f} \frac{q_s^0(n_1 \dots n_f, k_1 \dots k_f) p_s^0(k_1 \dots k_f, m_1 \dots m_f) - p_s^0(n_1 \dots n_f, k_1 \dots k_f) q_s^0(k_1 \dots k_f, m_1 \dots m_f)}{(\nu_0(n_1 \dots n_f, k_1 \dots k_f) + \nu)(\nu_0(k_1 \dots k_f, m_1 \dots m_f) + \nu)} \quad (1)$$

where f is the number of degrees of freedom of the system, m the mass of the electron and q_s^0, p_s^0 are the unperturbed canonical matrices corre-