

THE HYDROGEN ATOM

Thesis by

R. M. Langer

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy.

California Institute of Technology

Pasadena, California

1927

THE HYDROGEN ATOM

by

R. M. Langer

Dissertation

Submitted to the Board of Examiners of the California Institute of
Technology according to the requirements for the degree Doctor of Philosophy
in Physics.

1927.

THE HYDROGEN ATOM

by

R. M. Langer.

ABSTRACT. A critical examination of dispersion theory indicates that a measurement of the refractive index of atomic hydrogen is important for the theory of matter. Such an experiment is fully described and discussed. The result is that $\mu_H^2 - 1 = (1.38 \pm 0.26) \times 10^{-4}$. Incidentally, it is found that a partial pressure of half a millimeter of atomic hydrogen can be had in a discharge tube while the discharge is on. Thermal conditions in such tubes are discussed and investigated.

The experimental result is at first sight not in support of the new quantum mechanics which requires $\mu_H^2 - 1 \approx 2.3 \times 10^{-4}$. However, by assuming that $\psi \bar{\psi}$ is connected with volume, in the kinetic theory sense it turns out that the expectation from the theory is effectively $\mu_H^2 - 1 \approx 1.5 \times 10^{-4}$. This leads support to the physical reality of the quantity $\psi \bar{\psi}$ and leads to a prediction of an increase in refractivity at very low pressures for almost any gas. Pictures are given of the normal hydrogen atom and also its excited states and of the configuration under the action of a light wave.

One of the most impressive features of classical electrodynamics is the ease and directness with which the phenomena of dispersion can be explained. The laws of dependence of the refractive index on frequency, density and temperature can be described very successfully and the relation derived connecting refractive index with dielectric constant is indeed a triumph for the theory. In fact so sound are the foundations of the theory that it has become a test of hypotheses of the structure of matter.

The notions of atomic structure developed according to the quantum theory as it stood up to about a year ago have failed in this test and for that reason as much as for any other they are being discarded. The failure consisted chiefly in the fact that the frequencies ν_i calculated from the formula

$$\mu^2 - 1 = \frac{e^2 N}{\pi m} \sum_i \frac{f_i}{\nu_i^2 - \nu^2}$$

as derived by Sommerfeld, Epstein, Debye and others on the basis of the older quantum theory were not in agreement with the observed frequencies of anomalous dispersion.

This difficulty was so keenly felt that guided largely by a formula proposed by Ladenburg and improved by Kramers a new quantum theory was formulated to adjust the matter. I mean to say that the matrix theory of Heisenberg, Born, and Jordan, is almost equivalent to assuming at the start that the atom is composed of harmonic oscillators which are known to give anomalous dispersion at the frequencies which they absorb or emit. The quantum condition

$$p_q - q_p = \frac{h}{2\pi} \pm$$

is merely a matrix statement of the rule which Kramers showed led to a satisfactory dispersion formula.

The method of Schrödinger is not so brutally direct in achieving the same result. On that account alone it is to be preferred. It has also the advantage that instead of considering just the energy relations involved in the problem, it gives description of the whole process. In other words it states the distribution of electric charge as a function of time and space under the action of the electric field of a light wave and permits the calculation of the resulting electric moment and connects this with the refractive index as in the classical theory. It is in fact the first serious attempt at a complete detailed account of the matter. Our formulae have heretofore

phenomenological laws with qualitative justification on the basis of models which no one believed. The theories proposed in the past contained always more or less arbitrary quantities which were determined only by experiment. The Schrödinger mechanics however, makes bold to predict quantitatively, all observable facts of dispersion (perhaps anomalous dispersion is not to be insisted on too strongly). Where as the explicit expressions involving density, temperature, frequency, field strength, etc., have not been published as yet, the principles according to which they can be derived, are known. It must be emphasized that we are now for the first time in position to use all quantitative experiments as a test of the theory.

However, in attempting to take advantage of this possibility, one finds that so far only one case has been sufficiently treated theoretically. This case is the hydrogen atom in the normal state. This state of affairs makes the experimental determination of the refractive index of atomic hydrogen a matter of considerable importance.

What follows is an account of such an experiment together with a discussion of its relation to the theory. First, the principle of the measurement will be given and then mention will be made of several schemes to carry it

out. The method chosen will next be described and the result stated and analyzed especially from the point of view of precision and reliability in the face of the many spurious effects which play a part. The observational evidence will be compared with the predictions of the theory of Schrödinger and conclusions will be drawn as to the structure of the hydrogen atom and as well as to the interpretation to be placed on the quantity which is called charge density in the new mechanics.

PRINCIPLE OF THE MEASUREMENT.

In the determination of the refractive index of a gas there is no apparatus comparable with the interferometer. Which form is most convenient depends on the particular problem involved but the principle of the measurement is the same for all, namely - the optical path of a beam of light traversing a geometrical distance L in a medium of refractive index μ is μL . A change in optical path is indicated in an interferometer by a shift of fringes. If one path is kept constant and another changed by $\Delta(\mu L)$ then the fringes due to the superposition of a monochromatic beam of wave length λ which has traversed one of these paths on a coherent beam which has traversed the other,

will shift according to the equation.

$$\Delta N = \frac{\Delta(\mu L)}{\lambda} \quad (1)$$

where ΔN is measured in fringes. As ΔN , λ and L are easily observable quantities $\Delta\mu$ is readily computed. If we have a value of μ_0 for comparison then any other μ is known. The reference is furnished by taking μ for a vacuum equal to unity.

In the experiment under consideration only the roughest sort of numerical value can be hoped for. We may at first disregard the minor departures from the standard laws and making the approximations that are allowed because

μ is close to one we may write, if ρ is density and T temperature

$$\frac{\mu-1}{\rho} = \text{constant} \quad (2)$$

and

$$\frac{d\mu}{dT} = 0 \quad (3)$$

If then, the fringe system is determined by a certain length of path containing molecular hydrogen at pressure p , on changing a known fraction of the molecules into atoms, a shift will be produced according to an equation which can be deduced from (1) and (2); namely,

$$\Delta N = \frac{L}{\lambda} \frac{273}{T} \frac{p}{760} \left[2(\mu_H - 1) - (\mu_{H_2} - 1) \right] \quad (4)$$

where L is measured in cms if λ is measured in cms, p is the initial pressure

of molecular hydrogen in mms, T the temperature at which it has the pressure p (the volume being assumed invariable) and where δ is the fraction of hydrogen which is dissociated. The quantities μ_{H_2} and μ_H are the refractive indices of molecular and atomic hydrogen respectively under standard conditions, i.e. 760 mm, 0°C .

The Jamin ^{and} or the Michelson interferometer are both suitable for the determination of the quantities in (4), especially because they permit large values of L and therefore give high sensitivity.

Possible Methods.

The main difficulty in the experimental technique is to produce the sufficient atomic hydrogen and keep it long enough to make the measurements. Perhaps the most attractive means is to use high temperatures to produce the dissociation. We can calculate the dissociation as a function of the temperature from the equation of van t'Hoff

$$\frac{d \log k}{dT} = \frac{Q}{RT^2}$$

where k is the equilibrium constant of the reaction $H_2 = 2H$, i.e.--

$$k = \frac{H^2}{H_2} = \frac{4\gamma^2}{1-\gamma} p$$

Using the specific heats and entropies of atomic and molecular hydrogen given by Lewis and Randall, we can integrate the equation and get:

$$-RT \log k = Q_0 - 3.5 T \log T + .00045 T^2 + 1.17T$$

where Q_0 , the heat of dissociation of molecular hydrogen is now known definitely

to be very close to 105,000 calories per mole. This equation shows that for a pressure of 1 cm, dissociation begins to become appreciable at 2000°K and at 2500° most of the molecules are broken up. Duffendack has designed a furnace which attains such temperatures and with it he has produced dissociation in hydrogen and other gases. With such a technique in mind, preliminary experiments were carried out to find whether interferometric measurements could be made under conditions where violent convection was taking place. Whereas a great deal could be done by judicious arrangement of the apparatus, still it was found that the fringes were too unsteady for accurate reading in tubes subject to temperatures of only a few hundred degrees over room temperature, and results were so discouraging that this method was given up. If the convection of gas were the only difficulty involved, it might have been worth while

to continue, but it was found that the construction of even small furnaces was a matter of considerable difficulty, and calculation showed that with short paths and intense extraneous illumination and temperature gradients in the optically flat windows which were necessary, the sensitivity that could be expected was hopelessly low.

Methods which involved the production of atomic hydrogen in one vessel and measuring it in a connected vessel through which it was made to stream were regarded as unreliable because of the difficulty of measuring pressure, density, and concentration of atomic hydrogen.

The yield which can be obtained from collisions of the second kind with excited atoms such as mercury, proves, in cases which have so far been reported, to be so small that the effect on optical path length would be negligible.

The only other methods known for the production of atomic hydrogen in considerable concentrations are through the agency of electric discharge.

The information^{ation} as to the action of the discharge on the hydrogen gas has heretofore been of a qualitative character. Yet conclusions can be drawn

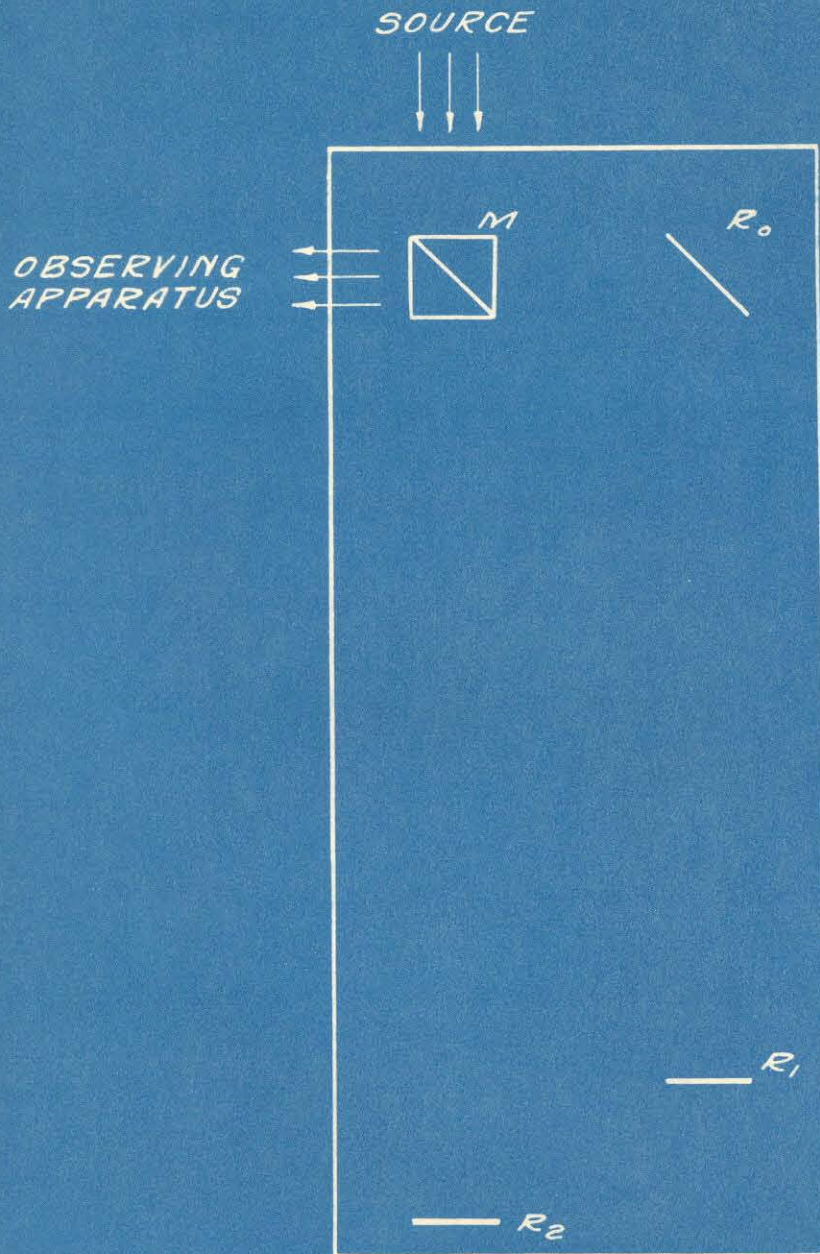


FIG. 1

THE INTERFEROMETER

that are reliable. It is known with certainty that the Balmer spectrum is due to the atom and the many lined spectrum to the molecule. The conditions under which the atomic spectrum is strong are just those which from chemical reasoning are favorable for the existence of the atomic form. In the sense of Born and Frank energy sinks (catalysts and reducible substances) must be absent in order to prevent the escape of the heat of dissociation when two atoms come together. The experiments of Wood, Bonhoeffer, Mohler, Urey and Smallwood, have shown conclusively that atomic hydrogen is present in large concentrations in discharge tubes showing the pure Balmer spectrum at pressures of the order of one mm.

It was decided therefore, to use the electric discharge as dissociating agent devising conditions and apparatus to avoid as far as possible the disturbing factors involved.

EXPERIMENTAL

A. THE INTERFEROMETER used finally was a modification of the Michelson type. The optical arrangement is shown diagrammatically in figure I. The

paths are somewhat over a meter long. An important feature is the fact that the two beams produced by the splitting device M are made parallel by the mirror R_0 . M and R_0 were rigidly fastened to a heavy steel base while R_1 and R_2 were supported by two plates which were each held by springs against three adjusting screws. Distances were calculated so that small adjustments of the screws behind R_1 and R_2 were sufficient to equalize the two paths so that white light fringes could be found. The mirrors were about 10 cm above a thick reinforced concrete slab in some of the work, and a ribbed cast iron surface plate in the rest. These rigid bases which were approximately 10 x 70 x 150 cm rested on three rubber or felt pads (1 inch sheet rubber was better than felt and the iron base was better than the concrete).

In trying various ideas for the elimination of convection, for the application of cooling agents, etc., other arrangements of the optical paths were used. Sometimes they were at right angles to each other, and sometimes one was made vertical by mounting one mirror on a four inch pipe. But the disposition in **Figure I** is vastly superior to all the others both in ease of adjustment (which is not an easy matter in an instrument of such size) and in steadiness of fringes.

In this latter property this scheme is like the Jamin interferometer for the paths are everywhere close together and are almost equally affected by disturbing influences such as vibrations, air currents, differential thermal expansion, etc.

B. THE DEVICE M, used instead of compensating plane parallels, is a novelty which is strongly recommended especially when specially made instruments are used for which adjusting appliances are not available. It consists of two matched prisms cemented together on their largest faces with Canada Balsam. Before cementing, one of these faces is coated with a half reflecting film. The prisms must be matched to the extent that their refractive indices must be equal for all wave lengths and the angles marked α in figure 2 must be closely equal. This is accomplished best by working with one stick of double height and sawing it in two after polishing.

About a dozen such cubes have been made up of glass and quartz and the following process was found to be easy after a little practise. A uniform semi-transparent film is coated on one prism and after making sure that there are no particles on the diagonal faces a drop of thick Canada Balsam is put on one and

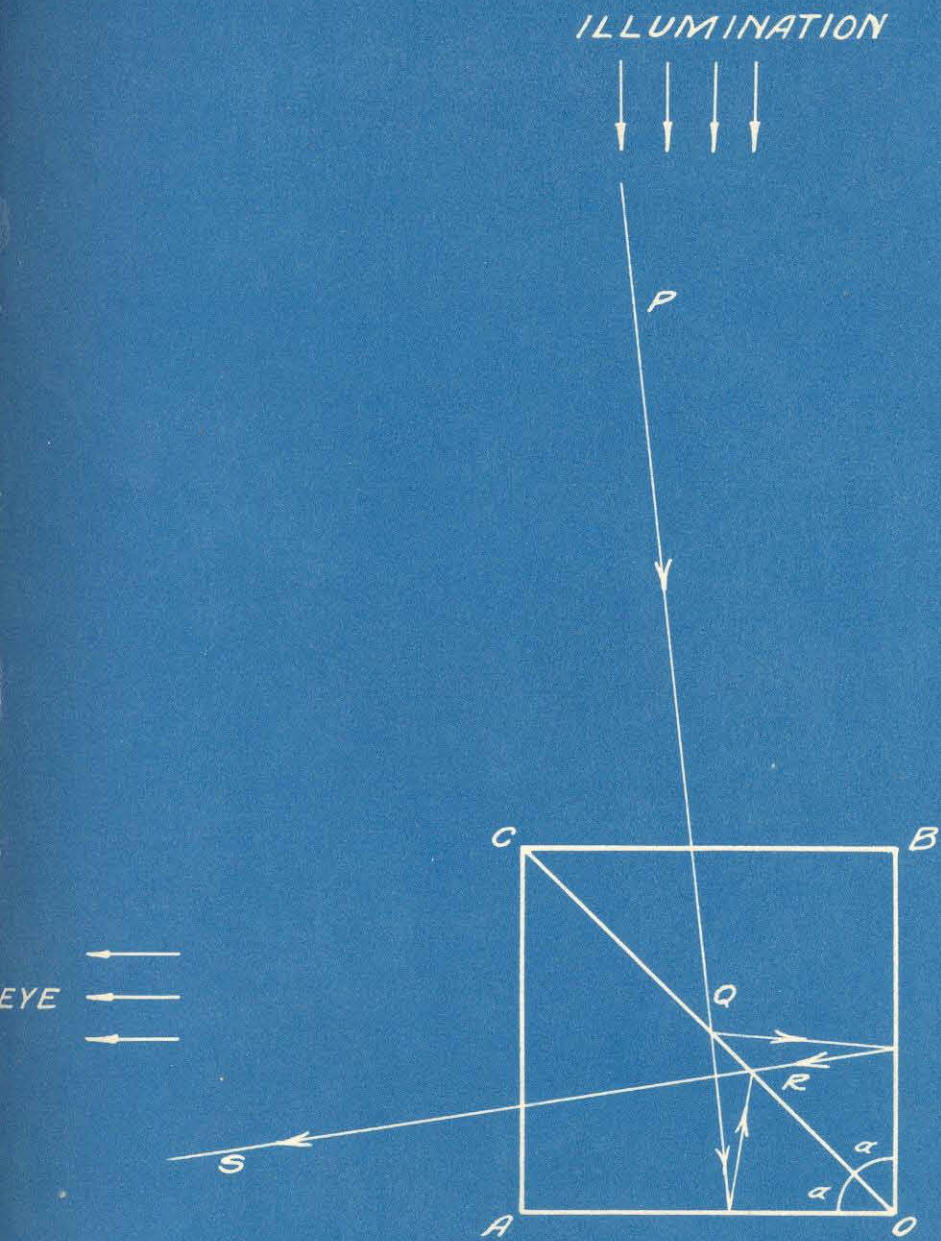


FIG. 2

the two prisms pressed together with as much force as ones arms can supply. The block is warmed gently on a hot plate to about 50°C turning it over and over to equalize temperatures as much as possible. In this stage the solvent of the Canada Balsam is driven off while the film is kept liquid. When the faces are all about as hot as the fingers care to handle the face OA is made perpendicular to OB. The condition that one wishes to fulfill is that any incident ray such as PQ is equally divided by the face OC and after the separated rays have travelled over exactly equivalent paths they are joined again at some point R into a single ray RS. When this condition is obtained, the eye will see white light fringes when the illumination is placed as in the figure. To bring this about, a weak monochromatic source with a somewhat weaker white light background is used. Focussing the eye on the face OB and getting the edges at O superposed the prisms are pushed around until monochromatic fringes are seen. The block is permitted to cool somewhat so that one must exert appreciable force to move the fringes. If the filter becomes too stiff the block must be warmed slightly on the hot plate from time to time. Pressure is applied to make the fringes move until the white light fringes appear. The search should not take fifteen minutes. When they are in view the block is allowed to become cold adjusting their position and direction

at frequent intervals. When cold the fringes hold their position (if they have been adjusted properly, while cooling) for months without much creeping.

The device has the following unusual advantages:

(a) All rays are compensated in a single piece so that repeated adjusting after each change in apparatus is unnecessary.

(b) It is the most economical in light losses, since there is the minimum number of air-glass transitions, and all are at approximately normal incidence, and since it is unnecessary to make a heavy coat to get rid of false reflections.

(c) The semi-reflecting film is protected from deterioration by chemical or mechanical agents and the troublesome process of getting a good coat is done once for all.

(d) There are no false images. The reflections from O_A and O_B are easily disposed of by making α different from 45° or simply by using a telescope or other observing apparatus which is focussed on the proper fringes.

It is a relief to get rid of this annoyance.

(e) No holder or adjusting screws are required. A bit of soft wax or a light spring keeps it in place since it is a geometrically stable figure.

(f) It constitutes without any auxilliary parts a remarkably simple and rugged Michelson interferometer. It can be held in the hand and passed around.

There may be some applications of the Michelson interferometer which it will not serve, in other respects it may be more ^{than plane parallel plates} versatile. It should be mentioned that crystalline prisms can produce double sets of fringes which may become mixed up under some conditions of use. In these cases it has been found useful to separate the fringe systems with a Wollaston Prism or to eliminate one set with a Nicol.

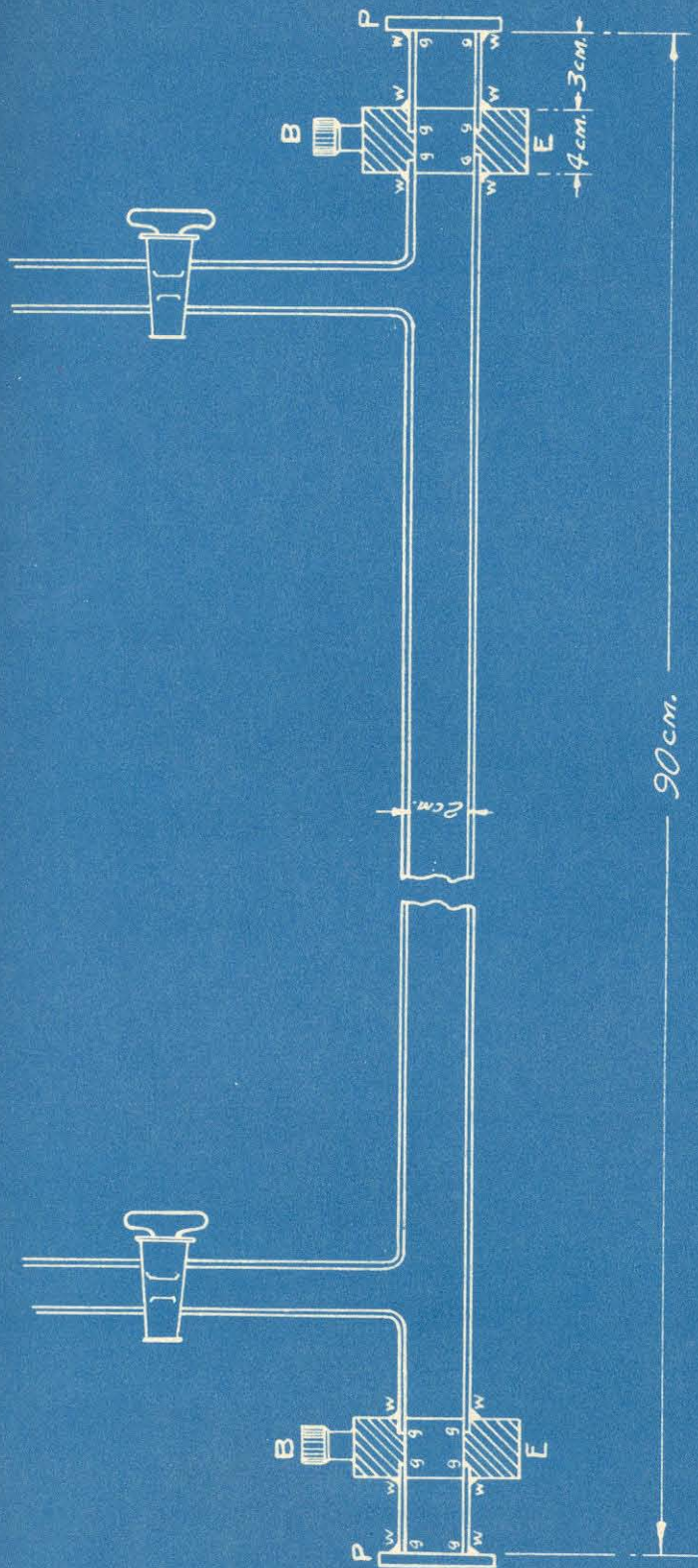
C. THE DISCHARGE TUBES. In the final state of the apparatus, the two arms of the interferometer of figure I contained identical tubes. In the process of development a great variety of shapes, lengths and other features was tried with special ends in view. Thick and thin tubes were tried coiled in all sorts of ways. Large and small aluminum, platinum and copper electrodes were tried. Outside sheet metal and mercury electrodes were also used. Several tubes were shaped to fit completely into cooling baths and in order to try liquid air, ^{one} was made to go inside a specially made Dewar flask with a hole thru the bottom for observation. This was a masterpiece of Mr. Clancy's art and I regret very much

that the only thing it accomplished was to produce spurious effects which wasted a great deal of time before their true nature was discovered.

The shape designed at the last is shown in figure 3. It is a cylinder of specially selected straight pyrex tubing, varying from 60 to 90 cm in length and from 0.6 to 2.5 cm in internal diameter. The side arms are short capillary tubes which can be closed by stopcocks a few centimeters from the main tube.

The electrodes E are large aluminium discs or cylinders through which a hole, bored equal in size to the internal diameter of the glass tube. The electrodes are waxed to the discharge tube and beyond their outside face a short length L of glass tubing continues the discharge tube a few centimeters. On the ends of these pieces are waxed the matched optically plane parallel plates P. B represents a binding post.

Two such tubes were mounted in the interferometer arms by means of wax or V-blocks. They were accurately aligned so that all the field was visible out to very nearly the walls of the tubes. Connections were provided from one tube to another, to the source of hydrogen, to the pump, pressure gauge, etc. Various auxiliary devices were attached directly to the center of the discharge tube on different occasions with the object of determining the pressures and temperatures



E = ELECTRODE
 B = BINDING POST
 W = WAX
 P = OPTICAL PLATE
 g = GROUND END

FIG. 3

DISCHARGE TUBE

in the discharge. The most successful will be described later.

This particular structure of tube was devised for the following benefits:

(a) The parasitical volume was negligibly small so that when the stop-cocks were closed the average density remained constant regardless of temperature changes.

(b) By putting the electrodes around the tube instead of off in side arms, one could look through all of the gas so that the special temperature conditions which are found to prevail at the electrodes play a part in the optical path. In this way density gradients along the tube are prevented from having any influence on the fringes.

(c) It is essential to be able to view all parts of the cross section of the tube in order to be able to take into account the temperature and density gradients at right angles to the line of sight.

(d) The pieces L had to be added because of the effect produced by the canal rays which streamed for some distance through the hole in the electrodes.

(e) Connecting tubes of equal length were necessary in order to equalize dispersion in the two arms and thereby permit the use of white light fringes with a central black fringe. For the same reason the end plates of the two tubes

had to be optically equivalent.

(f) The small area of metallic surface presented by the electrodes to the gas greatly reduced the catalytic recombination of the hydrogen atoms. The increased heating effect was taken care of by the large bulk and surface with consequently high heat capacity and heat dissipative power of the Al cylinders or discs. The fact that most of the Al surface was exposed to the air outside helped in heat dissipation and permitted cooling with moist cloths. By this means it was found that Wood's suggestion to have very long tubes so that the electrodes would not affect the center of the system was unnecessary and whereas two meter tubes with large metallic surface were found to be blue for a considerable distance from the electrodes, these tubes gave pure Balmer spectra right up to and through the hole in the electrode.

These points will be considered again later.

D. THE ELECTRICAL SYSTEM. The binding posts B in figure I were connected to a large condenser with an adjustable spark gap in series. The capacities used went up to about .01 mfd. The condenser was charged by high voltage transformers, some of them giving as high as 25,000 volts. Most of the results, however, were obtained with a 10 KVA transformer giving 16,000 volts at 50 cycles. choke

coils and series resistances in the primary regulated the power and the voltage. Condensed discharge was most frequently used, but the spark gap could be closed and uncondensed discharge was thoroughly investigated. Attention should be called to the fact that contrary to common opinion a condenser in series with a discharge tube frequently improves the performance of the transformer by raising the power factor in the secondary. It is surprising to observe the increased intensity that one may derive from a small transformer by putting in the proper capacity. Moreover since the discharge is not condensed there is no perceptible broadening of the lines.

Ammeters and voltmeters were used on the high side and in addition to these a wattmeter was used on the low side, so that some idea of energy and field intensity could be obtained.

E. ~~THE~~ OBSERVING APPARATUS was sometimes visual, sometimes photographic.

The illumination was provided by a high current density carbon arc (20 - 35 amps in 1/4 to 1/2 inch carbons) or else by incandescent lamps using as much as two thousand watts. Mercury light was also used but could not be had in the intensity of the arc. The matter of intensity was extremely important; first, because of the many extra glass-air transitions (probably 30 or more) in addition to the

usual losses in the imperfect reflectors and the unavoidable waste in the half silvered film of the interferometer. The second reason for high intensity is the unfortunate brilliance of the light reflected from the walls of the tube. This nuisance could be reduced by having parallel light. To achieve ^{this,} the source (which was extended and therefore required no lens) was placed at great distance (up to 10 metres) from the apparatus and the beam diaphragmed down in several places to just the size of the tubes. A third cause requiring high intensity was the unavoidable presence of the light from the discharge tube. This source had every advantage over the proper source except intrinsic brilliancy. Because of this extraneous light it was impossible to observe reliably without color filters except with a most brilliant arc. It was mainly on this account that observations were made with spectroscopes and spectrographs. For then one could attend to a part of the spectrum which was not illuminated by the hydrogen discharge. A further advantage was the possibility of observing the fitness of the tube by the purity of its spectrum. However, one had to sacrifice the view of the whole field at one glance and therefore all methods of observation had to be tried in turn. The lavish use of diaphragm is to be highly urged for such work. Two or three were used between the source and the dividing arrangement M and one

was placed near each mirror and others distributed wherever possible in the beam beyond the interferometer. Their importance in improving the visibility of the fringes can hardly be overestimated.

For direct visual observation a home made telescope was used. Since the black band of a white light fringe system was being observed one could focus on the mirrors R_1 or R_2 and use spots or etched lines on these mirrors as fiducial marks from which to judge the shift of fringes. This scheme rendered immaterial any relative motion between the interferometer and the telescope or eye. Color screens were also used to eliminate the hydrogen discharge and to clarify the fringes. If one had a very sharp filter that did not coincide with the hydrogen lines the improvement was astonishing and the precision of a reading was tripled at least.

In using a spectroscope or spectrograph the fringes are focussed on the narrow slit at a distance determined by the size of the image desired. One can use the cross hairs of the spectroscope or a fine wire across the slit as fiducial marks as well as the etched line mentioned before. The fringes are made horizontal and one sees through the instrument the spectra of the source traversed by a horizontal black line and by almost horizontal fringes. The

deviation of the fringes from the horizontal is a measure of the difference of dispersion of the gas in the two paths. When the discharge is turned on, the line spectrum appears superposed on the continuous background. But in a good tube, there is very little light due to the discharge between the Balmer lines, and one is hardly disturbed by the extraneous light, and it serves to indicate when the discharge is passing through the tube.

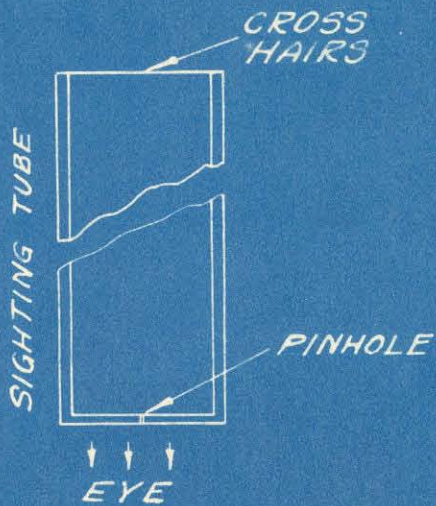
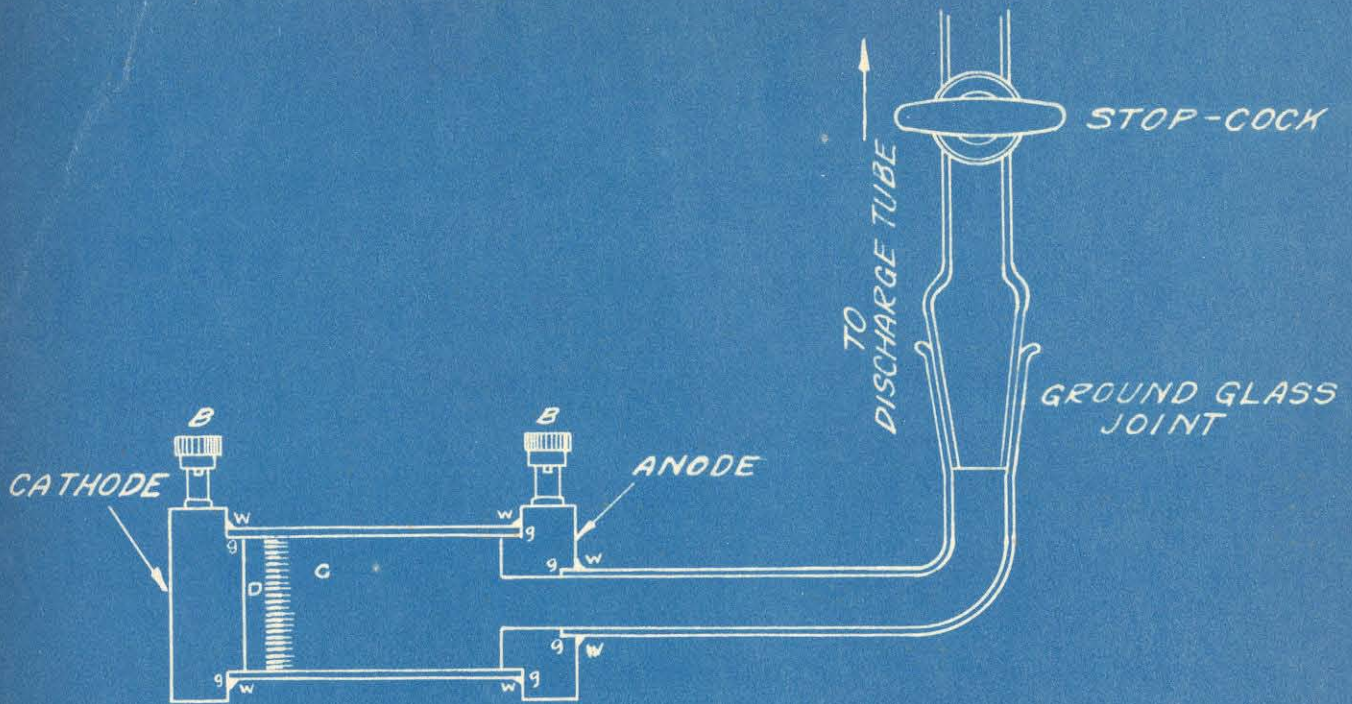
The photographic plates used were mainly, Ilford high speed panchromatic or Wratten and Wainwright panchromatic - the first mentioned being best of all in speed, smallness of grain, and flatness of sensitivity over the visual region.

F. AUXILIARY MEASURING APPARATUS. Besides electrical instruments already mentioned, several indicators had to be used. There was, of course, a McLeod gauge for pressure measurement, designed especially for accurate readings, in the range from .01 mm to several cms. This was accomplished by having a moderately small bulb, a couple of small auxiliary bulbs in place of a very long capillary and a moderate length of large capillary tube.

But it was unnecessary to rely on the McLeod gauge for the pressure.

The interferometer is a perfectly good instrument for this purpose and was

used almost exclusively for the determination of pressures used in calculations. By the same means and using atmospheric pressure, all volumes between stopcocks could be determined with extreme accuracy and these calibrated volumes used to expand gas from atmospheric pressure down to any lower pressure the final pressure being as accurately known as the ratio of the volumes. There was no difficulty then in ordinary pressure measurements or in adding known increments to the pressure, but the determination of pressure while the discharge was on (which was necessary to find the percentage dissociation) was quite another matter. Attempts were made to accomplish this with the McLeod gauge, with drops in closed end capillary tubes attached to the discharge and with rubber diaphragms connected to a minute mirror mounted so that a motion of the diaphragm produced a rotation of the mirror. None of these were pushed hard enough to warrant judgement on their virtues. Instead the interferometer itself was used for this purpose and also a dark space gauge shown in Figure 4. The ground joint and right angle bend enabled one to vary the tilt of the gauge until the face of the cathode was exactly at right angles to the sighting tube with which the distance from the cathode to the edge of the dark space was measured. The sighting tube was simply a tube of bakelite closed at the end towards the eye



D = DARK SPACE
 C = CATHODE GLOW
 W = WAX
 B = BINDING POST
 g = GROUND END

FIG. 4

DARK SPACE GAUGE

except for a tiny pinhole about 0.2 mm in diameter. At the other end two fine hairs were stuck on with shellac to make cross hairs. This tube was mounted on a comparator so that a motion parallel to the motion of the edge of the negative glow could be followed and read on a scale graduated to 0.1 mm. The voltage across the gauge varied from about 350 to 425 volts, it was supplied by a storage battery and was measured on a voltmeter in parallel with the gauge. A galvanometer in series gave the current flowing. The procedure in making pressure measurements with this gauge and with the interferometer, and the formulae involved will be taken up under another heading. The use of a dark space gauge was suggested to me by Sinclair Smith.

No accurate temperature measurement of the inside of the tube were made.

The calculations of temperature given later are considered more reliable and more significant than direct measurements at particular points.

G. PROCEDURE IN MEASUREMENT: For the determination of the fringe shift, due to the passage of the discharge, all stopcocks were closed so that no change in density could take place, the fringes were watched or photographed under

quiet conditions with no discharge. The discharge was now flashed on and a sudden jump of fringes was looked for. In order not to heat the tube unduly, the discharge was kept on only for an instant. A jump in fringes was looked for again when the discharge was snapped off, this procedure was repeated over and over again at all pressures from the lowest that the diffusion pump would give up to several centimeters. The power was varied from the smallest that would pass through the tube to several kilowatts. Frequencies of 25, 50, 60, 250 and 500 cycles were employed. All available light sources were used in turn. Moist hydrogen, collected over water from a tank, or generated by electrolysis of NaOH, nitrogen, air and helium were placed in the tube. Wavelengths from about 4300 to 7900 Å were used in illumination. Attendant conditions of the discharge tube, vibrations in the neighborhood, presence of mercury vapor or its absence were taken into account, (current voltage and power were all observed). The sensitivity of the visual observation was estimated by using mechanically produced and calibrated fringeshifts. On the photographic plate, the shift of the fringes with respect to the fiducial mark, was measured with a comparator for several wavelengths in different parts of the spectrum. Any peculiar behavior of the fringes was verified and observations repeated until

the cause had been tracked down. So large a number of observations were taken (many thousands) and so great a variety of conditions were imposed and so carefully were these conditions analyzed, that there is no question but that the full behaviour of the fringes was completely understood and that the results which will be stated later are reliable statements of facts, no matter what conclusions are derived from these facts.

The pressure measurements with the interferometer were made by opening the stopcock between the two tubes (all others being closed) and passing the discharge through one. Gas flowed from this one into the other because of dissociation and temperature increase. The shift in fringes accompanying this change in density was measured. At the same time the power in the electrical circuit was measured. In the case of the dark space gauge, the edge of the dark space was sighted without the discharge, all stopcocks being closed, excepting the one between the discharge tube and the gauge. The discharge was now passed and the power noted. The change in dark space determined the pressure.

Temperature conditions were observed by the motion of the fringes in different portions of the circular field. From this motion the density distri-

bution could be deduced, and from it the temperature distribution. Another means of making a temperature estimate was to measure the pressure change with the dark space gauge using helium in the tube, in this case no dissociation could take place and the change in pressure was determined only by the average change in temperature. Along with these temperature measurements, the regular fringe-shift measurements (all stopcocks closed) were made for the determination of index of refraction of atomic hydrogen, and all discharge conditions etc., were observed and correlated.

RESULTS.

When all accidental shifts are avoided as far as possible, and when account is taken of those which remained in certain unimportant limiting cases, the fringe-shift due to the change from molecular to atomic hydrogen is zero. In other words, according to equation 4, the refractive index of atomic hydrogen under standard conditions is one-half that of molecular hydrogen. Numerically at about 6000 Å

$$(\mu_{H_2} - 1) = \mu_H^2 - 1 = 1.38 \times 10^{-4}$$

Another way of putting this is to say that the effect of two hydrogen atoms on a light wave which does not coincide in frequency with an absorption line is the same whether the atoms are united to form a molecule or are free to move any distance from each other. This result is quite in accord with the ideas of some chemists who feel they have evidence showing that the hydrogen molecule is just a pair of loosely associated hydrogen atoms. It is also in accord with the spectroscopic evidence of the similarity between the radiation from molecules and the line spectra of the atoms of which they are composed. This similarity has led to the assumption that there is a permanence of quantization of electrons when their atoms combine to form molecules. Although since there are energy changes involved in the warping of the charge distributions, one cannot expect the refractive index to remain quite unchanged still since the heat of the association is small compared with the electron energy, the change in refractive index should be fairly small.

The exact equality between $\mu_{H_2} - 1$ and $2(\mu_H - 1)$ cannot of course be concluded from these measurements. It will be obvious that the possible difference is determined by the accidental effects which have persisted in our observations, by the precision of the observations, and by the quantity of

atomic hydrogen which was present in the tube while the observations were being made. The numerical value of this difference will be estimated later

on. The final result will be that we may write $\mu_H^2 - 1 = [1.38 \pm .26] \times 10^{-4}$.

The second result of the experiment is that in a properly arranged tube, free from reducible substances and using moist hydrogen at pressures in the neigh-

borhood of 1 mm. so that pure Balmer spectrum is obtained, concentrations of

20 percent or more may exist over periods of time of .01 of a second. This

has, of course, been observed before and it is not surprising that under condi-

tions suitable for the excitation both of molecular and atomic hydrogen that

when only the atomic spectrum is shown, there should be a considerable frac-

tion of atoms. In fact, I think it is perfectly sound to conclude that under

these conditions, the absence of the molecular spectrum while the discharge

is passing, shows an absence of molecules during this time. Since the resonance

potentials of the two systems are so close to each other, and since as far as

we know, there are no metastable states, the probability of excitation must be

comparable, and there is no means of explaining the quenching of the molecular

spectrum other than the absence of the molecular form. How long the atoms

persist after the dissociating agency of the discharge has been removed is another

matter. But from the chemical kinetics of Born and Franck, and from numerous experiments of Wood, Bonhoeffer, Urey and Smallwood, and others, we believe that the homogeneous recombination of hydrogen atoms is a slow process compared with the intervals of .01 or a second or less between discharges. Some data on the rate of this reaction is had in the measurements with varying frequency, but it is rather too sparse to provide definite conclusions. However, the work is being carried on and a good value for the rate of reaction is looked for by such measurements.

The third result worth mentioning is the fact that the pressures which exist in discharge tubes are of the order which could be calculated from the increase in temperature, due to the energy supplied to the tubes. Quantitative results are not very precise, but they are sufficient to answer a doubt which is very common as to whether one may define temperature in a discharge tube or whether the existence of numerous high velocity particles, moving under the action of electric field, destroys the usefulness of this conception. The answer is, that if one uses the gaslaw

$$PV = NRT$$

to determine temperature from the pressure, then the temperature is a perfectly definite thing.

ANALYSIS OF THE OBSERVATIONS.

A. **SPURIOUS EFFECTS.** It is considered essential to discuss before anything else, the possible undesirable effects and to show how they were taken into account. Of the many people with whom the results have been discussed no one has brought up a possibility which has not been considered. Moreover, the fact that in the final design no measurable shift was obtained over a wide range and variety of conditions gives one considerable confidence in the belief that nothing of importance was neglected. Follows a list of difficulties which may perhaps are peculiar to this particular application of the interferometer.

I. Motion of gas into side arms. The volume not included in the light path was only about five percent of the total. If the main tube was 100°C above room temperature and the side arms at room temperature (this is an extreme case), the relative density would be 4 to 3. If the subscript refers to the large volume and 2 to the small and 0 to the initial state, we may write

$$\rho_1 = \frac{3}{4} \rho_2$$

and

$$0.95 \rho_1 + 0.05 \rho_2 = \rho_0$$

whence

$$\rho_1 \doteq .99 \rho_0$$

showing that one hundred degrees difference makes only a one percent change in density and therefore by (2) in $\mu - 1$. This is far smaller than the precision of the experiment and can be entirely disregarded. The parasitic volume will then be considered zero in the case where all stopcocks are closed.

II Change in length of the tube due to thermal expansion when the discharge is turned on. In effect this reduced the optical path by substituting for air at atmospheric pressure, a gas at very low pressure.

$$\Delta N \doteq \frac{(1 - \mu_{\text{air}}) C L \Delta t}{\lambda} \quad (5)$$

where μ air at atmospheric pressure and 15°C is = 1.00027

λ = wave length or 6000 \AA

C = coefficient of expansion of pyrex = 3.6×10^{-6} per $^{\circ}\text{C}$

Δt = average change in temperature of the tube

μ = index of refraction of the gas in the tube

L = length of tube = 90 cm

This gives a shift of 1.4×10^{-3} fringes per degree change in temperature.

This is very small, even for extreme temperatures. Moreover the rise in temperature is gradual and would not at all interfere with visual observation even

if it were large since it was a sudden change that was to be looked for. In the photographs the exposure was only about one second in which time the change in length must have been small, especially considering that the tube heated only to a certain temperature and fluctuated only slowly and slightly from it when the discharge was turned on and off. Finally the change in length was measured by attaching the mirror R_1 to the tube which was fastened only at the other end. In this way the effective shift was multiplied over a thousand fold since the formula now is

$$\Delta N = \frac{\mu \Delta L}{\lambda} = \frac{CLT}{\lambda}$$

The shift before the tube reached equilibrium was a few fringes showing that the change in length was negligible in the case when only $(\mu - 1)$ was effective in producing a shift.

III Temperature changes along the length of the tube. Equation 1 is more properly written

$$\Delta N = \frac{1}{\lambda} \Delta \int \mu dL \quad (6)$$

since we have shown

$$\Delta \int dL = 0$$

we can write

$$\Delta N = \frac{1}{\lambda} \Delta \int (\mu - 1) dL$$

and from equation (2) if only temperature changes

$$\Delta N = \frac{\text{Constant}}{\lambda} \Delta \int \rho dL \quad (7)$$

ρ is here the average density over the cross section. Now the integral represents the amount of matter in the tube (since practically all of the tube is in the optical path) and is independent of temperature so that

$$\Delta \int \rho dL = 0$$

and $\Delta N = 0$ for this case.

IV Electrostatic effects. Several phenomena come under this head. It is conceivable that if the electric parts have large distributed capacity rigidly attached to the interferometer, the mechanical forces due to the attractions on induced charges, especially with such high voltages, may warp one of the arms more than the other. Such an effect was apparently observed under some conditions especially when external electrodes of large area were used. In such the high capacities were visible and could be removed or reduced. The characteristic features of the effect are its startling suddenness and its in-

dependence of the strength of discharge or pressure in the tube. This last point definitely showed that it had no connection with the properties of hydrogen and indeed it was found that He or air did just as well. At any rate it was noticed and disposed of.

Another possible effect is the change in μ with field intensity. This would not be expected to be important. It should be proportional to field intensity which was low. At most it was a few hundred volts per cm. when the voltage was on the electrodes and no current passing. When the discharge was on or between discharges it was of course, much lower. It should be proportional to pressure and therefore should be more noticeable at high pressures. It was looked for under these favorable conditions and found not to be appreciable.

V Heating of the plane parallel ends of the discharge tube. For a time the flat ends were waxed directly to the outside of the electrodes without the extension pieces L shown in figure 3. It was noticed that at low pressures a slow shift took place, in the direction of increasing refraction. The change was greater in the center than at the edges. On shutting off the discharge the return was slower than the original change. The magnitude of the

effect increased for a time as the pressure increased and grew rapidly immediately after the discharge was turned on and more slowly later on, reaching a steady value in about fifteen seconds. All these properties are characteristics of temperature effects. It was concluded that the heating was due to the bombardment of the ends by canal rays rushing toward the electrodes and passing on through the hole in them. This was plausible because the temperature coefficient refractive index of glass is sometimes of the order of a couple of units in the fifth decimal place, and a heating of the inside face could produce the effect observed. For example with a heavy flint glass, an average change of temperature through the plate of 1°C might produce with plates 2 mm thick (since there were two of them and the light passed through twice) a displacement of a tenth of a fringe.

The effect might have been removed by using at opposite ends, plates with temperature coefficients that had different signs. But the method chosen was easier and cheaper. With extension tubes L of two or three centimeters length the effect disappeared. One could see the red beam of canal rays streaming towards the end of the tube but stopping before getting there. However the small positive effect which was found at the lowest pressure may be attributed to this

cause. The mean path of canal rays at this pressure (about 1 mm) is usually much smaller than 2 cms but it must be remembered that in this case the rays were protons and of very small diameter.

VI Ions, Excited atoms and Electrons. It might be expected that these constituents could contribute to the refraction. In the usual case where condensed discharge was used they can be disposed of immediately because the excitation existed for such a short time; probably less than .0001 sec. It could not be blurred out perceptibly by a moving mirror with a time resolving power of that order of magnitude. After the excitation ceased the excited atoms and electrons would disappear in 10^{-7} sec. and the ions in 10^{-4} sec. It may therefore, be considered that they last only while the discharge is actually passing. Since this is only for a small fraction of the total time between successive discharges, any effect which they produce will be unnoticed by the eye or the photographic plate.

When ordinary discharge is used the current flows during most of the cycle but on the other hand the current density is less in the same proportion as the time is greater. Now the excited atoms in hydrogen under heavy discharge according to Ladenburg, Kopfermann and Carst are only about 10^{-4} of the total

number and since their value of $(\mu-1)$ away from absorption lines is not many times that of the normal atom, their contribution is nil.

It remains to estimate the number of ions and electrons. A great deal of experimental work has been done in this direction, some of which are probably less accurate than the following calculation.

If n is the number per cm^3 of charged particles carrying the current and v their average velocity then i the current density

$$i = nev \quad (8)$$

For the high current density of 1 ampere/ cm^2 this gives

$$nv = \frac{3 \times 10^9}{4.77 \times 10^{10}} = 6.3 \times 10^{18}$$

Now since the carriers under these conditions are probably all electrons or protons their velocity can hardly be under 10^6 cm/sec. and cannot be more than the velocity of light. Therefore

$$6 \times 10^{12} > n > 2 \times 10^8 \quad (9)$$

The limits could be narrowed easily and interesting conclusions could be drawn. Suffice it to point out that 6×10^{12} per cm^3 is a fraction of a per cent of the atoms in the gas at a pressure of 1 mm and since the refractive index of protons or electrons is low they are without influence on the measurement.

VII. Variation in density over the cross section of the tube. This is perhaps the most important disturbance. It occurs because of the temperature gradients which exist because the heat generated by the discharge escapes through the glass walls. If one starts with straight fringes then the discharge causes them to bow in the center of the field. The motion is in the direction of diminishing refraction in the center which is therefore of lowest density. A better method of observation is to start with the fringes curved just enough so that the discharge straightens with power and pressure. It never attains magnitudes of more than one fringe and can be reduced by means indicated by consideration of the theory of the effect.

Let us make the most unfavorable assumptions and say that the heat is developed uniformly through out the volume and that it is dissipated only by conduction. The first of these is not nearly true and is rather too conservative, for we know that the greatest voltage gradients are near the electrodes which have by far the greatest heat dissipating capacity. As a matter of fact any lack of uniformity of heating would provide faster cooling and would be advantageous for our conclusions. (An important example of such non-uniform heating is the ion and atomic recombination on the walls). The assumption that only conduction

is effective is of course only approximate. That it plays the most important part at moderate power is shown by the bowing of the fringes at very high power the temperature gradients are more effective in starting convection. Radiation accounts for only a few percent of the energy but even this much is important when it comes to calculating percent of dissociation.

Using the assumptions nevertheless, we can find the temperature gradients from the definition of thermal conductivity which says that if Q is the heat passing per second through unit surface and n the normal to it, then

$$-k \frac{dT}{dn} = Q \quad (10)$$

In this equation k is independent of pressure at least down to 1 mm.

In the steady state, which is soon reached, the heat passing every second through a unit surface on a cylinder concentric with the axis of the tube (disregarding the end convection) is the heat generated in unit length divided by the area per unit length

$$Q = \frac{W \cdot \pi r^2}{\pi r_i^2 L \cdot 2 \pi r} = \frac{Wr}{2 \pi r_i^2 L} \quad (11)$$

where W is the energy furnished to the tube, L the length, $2r_i$ the internal diameter and r the distance from the axis.

This gives from (10)

$$-\frac{dT}{dr} = \frac{W}{2\pi r_i^2 kL} r$$

whence

$$T_0 - T_r = \frac{W}{2\pi r_i^2 kL} \int_0^r r dr = \frac{W}{4\pi r_i^2 kL} r^2 \quad (12)$$

where T_r is the temperature at distance r .

It is seen from this that with a given energy density the difference in temperature between walls and center is proportional to the square of the diameter of the tube. With this in mind, some tubes were used with diameters of 6 mm. These tubes showed no temperature bowing until fairly high pressures.

From the gas law one can write

$$\rho_r = \frac{pM}{RT_r} \quad (13)$$

where M is the molecular weight of the gas, ρ_r is the density at distance r and p the pressure which is the same all over. The reciprocal of the density is quadratic in r which explains the bowing of the fringes and further the factor p shows why the effect increases with the pressure.

Calculation from (12) and (13) leads to the expression for ρ_r

$$\rho_r = \frac{W}{4\pi kL} \frac{\bar{p}}{\log\left(\frac{T_0}{T_0 - \frac{W}{4\pi kL} r^2}\right)} \frac{1}{T_0 - \frac{W}{4\pi kL} r^2} \quad (14)$$

$$\bar{r} = \frac{1}{V} \int r^2 dV$$

$$\bar{r} = \frac{I_2 - I_1}{I_3 - I_2} \cdot \frac{P}{T_2}$$

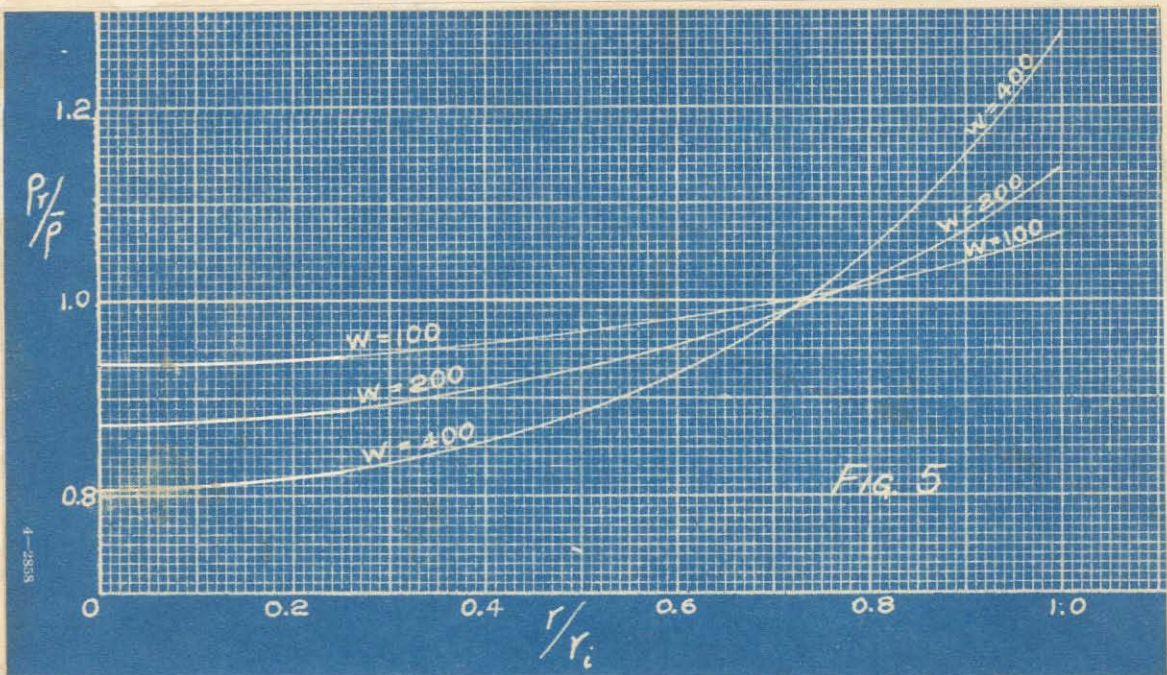


FIG. 5

change shift is very small and since it is easy to block out some portion of the field for radii larger than .6 of the total radius (indeed it is very difficult not to do so) by fixing attention on this portion the observation is free from disturbance due to density gradients. As a matter of fact the whole shift at a pressure of 5 mm and density of 400 water in the tube the shift is only two

where $\bar{\rho}$ is the average density which equals the initial uniform density and is given by

$$\bar{\rho} = \frac{2}{r_i^2} \int_0^{r_i} \rho_r r dr$$

(14) can be also written

$$\rho_r = \frac{T_0 - T_i}{\log \frac{T_0}{T_i}} \cdot \frac{\bar{\rho}}{T_r} \quad (15)$$

in which T_i is the temperature at the wall where $r = r_i$, i.e.

$$T_i = T_0 - \frac{W}{4\pi kL} \quad (16)$$

There must, of course, be a value of r such that $\rho_r = \bar{\rho}$. Since neither (12) nor (15) contains the p , this value of r is independent of the pressure. Moreover figure 5 where $\rho_r/\bar{\rho}$ is plotted as a function of r/r_i , shows that for all values of W the density is very little changed from the original density at from seven to eight tenths of the distance to the walls. Here the fringe shift is very small and since it is easy to block out some portion of the field for radii larger than .8 of the total radius (indeed it is very difficult not to do so) by fixing attention on this portion the observation is free from disturbance due to density gradients. As a matter of fact the whole shift at a pressure of 2 mm and energy of 400 watts in the tube the shift is only two

tenths of a fringe and convection makes it still less.

As the data given further on show, the photographic observations using thin tubes were not much affected by this cause up to pressures of about a centimeter, and knowing the cause it is possible and safe to correct for it, if desired, at the lower pressures which alone are important and in which the effect is very small indeed.

It must be felt from these facts that density gradients are not serious. Still a direct experiment was brought to bear which was free from the possibility of error in this respect. Unfortunately it was not started soon enough to be thoroughly developed else it would have been a sufficient means of clearing up practically all of the difficulties encountered in the measurement.

It was found that NaOH is one of the best catalysts for the recombination of atomic hydrogen to molecular. Accordingly in one of the tubes of the interferometer NaOH was distributed by allowing a dilute solution to enter and pumping off the water. The tubes were connected in series and the discharge passed through them with the stopcocks between closed, but the hydrogen gas at the same pressure in both. Now since they were thermally, electrically and optically the same in all particulars, the temperature changes, density gradients etc.,

were the same in homologous portions and in the interferometer used the changes in one would neutralize the changes in the other as far as fringe shift was concerned. But between discharges the recombination in the NaOH tube would be so fast that the concentration of atomic hydrogen in it would be zero and so any shift of fringes would be a measure of the refractivity of the atomic hydrogen in the other. No shift was obtained. Moreover on opening the stopcock between the tubes the passage of gas from the pure one to the other as indicated by the fringe-shift showed that considerable atomic hydrogen was present. The observations were not repeated often enough nor were the conditions varied enough to entitle this experiment to all the weight it might have deserved had it been properly performed. It will be continued.

B. THE ZERO SHIFT. Most reliance is to be placed on the photographic runs with the thin tube. Table 1 gives the average of twelve series of runs with pressure varying from 1 mm to over 2 cm.

Figure 6 is a graphical representation of Table 1. The procedure used in getting this data was to photograph the fringes in a very fast spectrograph (f 2.7 lens) first, without the discharge at the lowest pressure then with, then

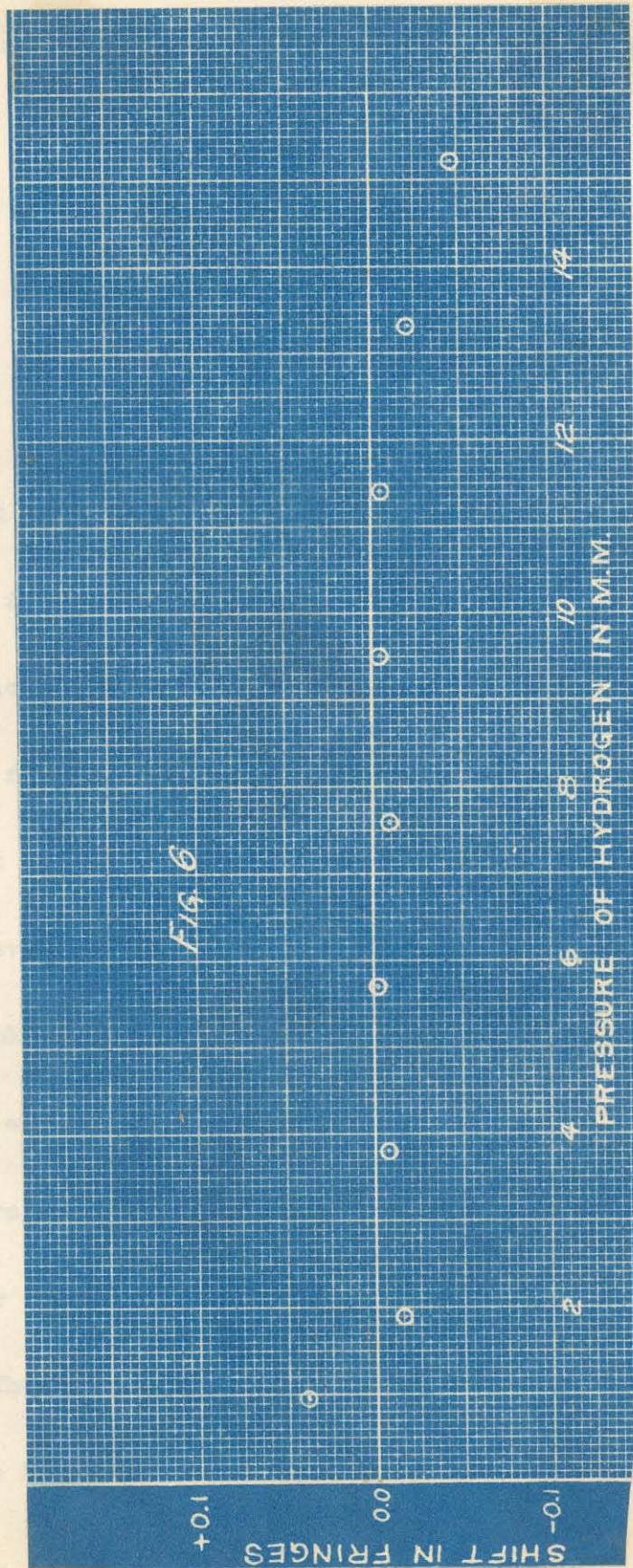


TABLE 1

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

then without, then with. These five exposures taken one after the other indicated any accidental drifts due to temperature changes, turbulence in the air vibration due to traffic nearby, leaks in the apparatus, etc., etc. Only such plates were used as were free from such disturbances. After the five exposures were made at the lowest pressure, gas was added and five more taken on a single plate which would have over fifty exposures.

The next plate would be under different conditions of exposure, energy, type of discharge etc., in all the variety that could be imagined.

Since there were from two to five fringes in the field each exposure provided from four to ten measures of the position (maximum and minimum darkness) of the fringes. The individual readings were just like the average in being close to zero, or at the high pressures slightly negative. It is not a matter of

finding a small effect hidden by larger accidental errors. Once in a while an apparent shift would be observed, but it would have all the earmarks of an accident. It would come where it shouldn't, it would not be repeatable and would have no connection with the discharge conditions. At low and high pressures this was not so, but the systematic errors in those cases have been explained. The plates were measured with great patience and is believed that the averages given are good to better than a hundredth of a fringe. In calculating the error of the experiment such precision will not be claimed in order to err on the safe side.

The visual observations being so much easier and quicker and subject to closer correlation with contemporary conditions were performed in greater numbers and variety. Here the reliability of a single observations is not so large because of the distracting influence of the electric sparks and the light in the tube and because of the fact that attention is divided between watching the fringes and closing the switch (this was sometimes done by a second person). The direct vision spectroscope most often used was a beautiful instrument (made by Schmidt and Haensch) giving high magnification and high dispersion so that the field of vision could be made almost free from light from the discharge and small shifts detected. The telescope too was always available so that after seeing the spectral condition of the tube in the spectrograph

one could immediately shift and observe the thermal conditions with the telescope. As one watches the fringes over long periods many motions are visible unless things are very quiet. Nevertheless a sudden shift correlated with the discharge is easily detected and distinguished from meaningless drifts. The practised eye notices a sudden change of a thirtieth of a fringe under favorable conditions. But a twentieth is hard to miss and a tenth can be very well estimated.

In saying that no shift was observed it is meant that taking all observations into account, including the photographic, the shift must have been less than 0.03 fringes. In order to estimate the possible error we shall assume that the shift was 0.03 fringes and see what effect that might have on the

$(\mu_H - 1)$ in equation (3).

C. CONCENTRATION OF ATOMIC HYDROGEN. Before being able to give a numerical value to the error, one must find the concentration of atoms at the moment the shift was being observed. This question has been investigated experimentally using the apparatus already described, but it is considered worth while to make a calculation on the basis of other experiments and it is believed that the results obtained are as reliable as those given by the experiments first mentioned.

Bonhoeffer has measured the rate of recombination of atomic hydrogen

and his measures at 0.5 mm fit exactly the law

$$\gamma = \gamma_0 e^{-k t} \quad (17)$$

where γ is the fraction of H_2 molecules dissociated and k the so-called specific

rate of recombination at 0.5 mm the value 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 (17)

$$\gamma = \gamma_0 e^{-2^{n+1} p^n t} \quad (18)$$

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

In some of 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 dis-

charges 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

$$\bar{\gamma} = 100 \gamma_0 \int_0^{\frac{1}{100}} e^{-2^{n+1} p^n t} dt \quad (19)$$

$$= \frac{100 \gamma_0}{2^{n+1} p^n} \left[1 - e^{-\frac{2^{n+1} p^n}{100}} \right]. \quad (19')$$

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 finds 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

PARTIAL PRESSURE OF ATOMIC HYDROGEN IN M.M.

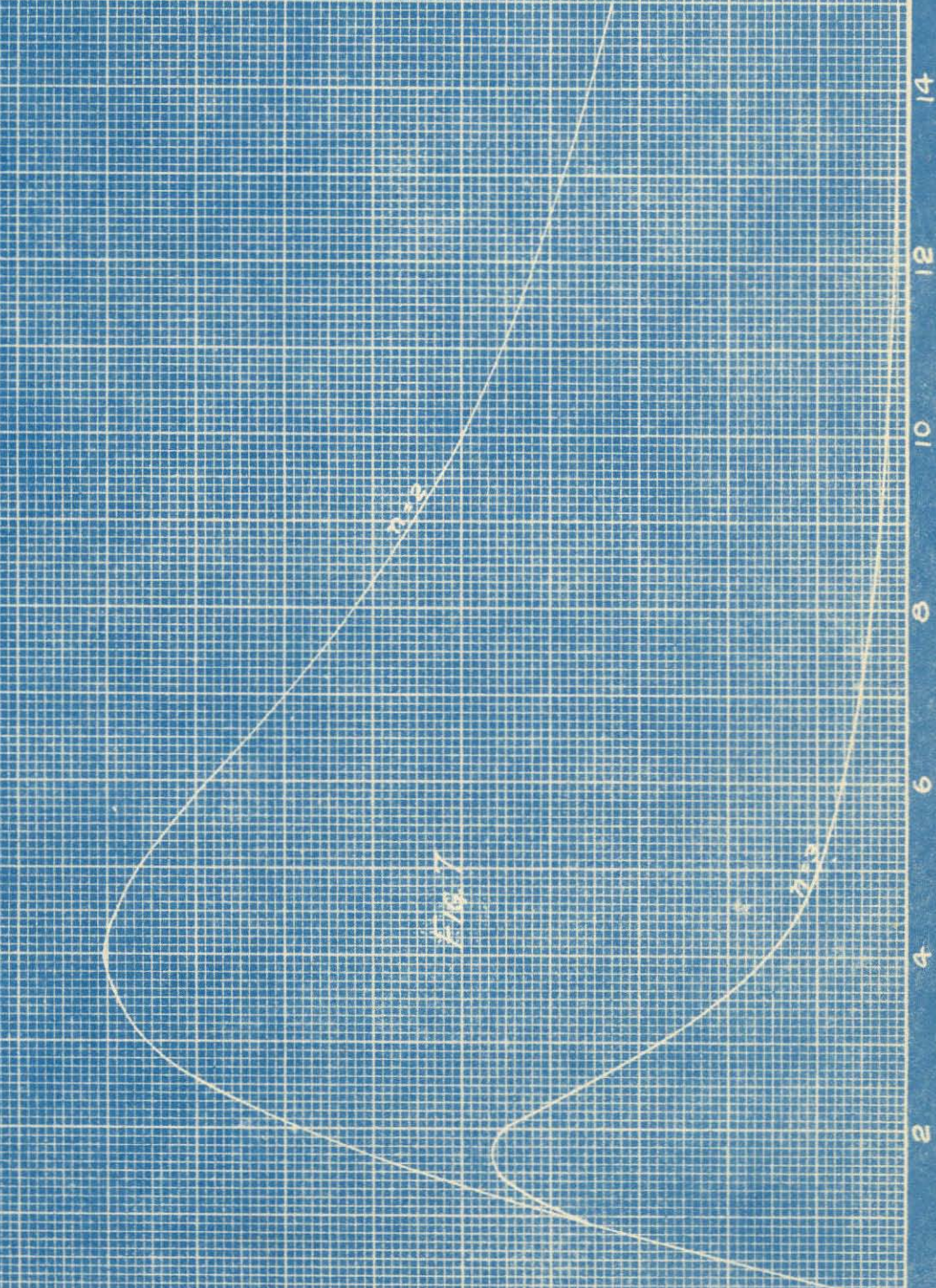
PRESSURE OF MOLECULAR HYDROGEN IN M.M.

0 2 4 6 8 10 12 14

0 2 4 6 8 10 12 14

er

di



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 (19')

$$\bar{\gamma} = \frac{10}{2^n p_{H_2}^n} \left[1 - e^{-\frac{2^{n+1} p^n}{100}} \right]$$

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

$$P_H = \frac{10}{2^{n-1} P_{H_2}^{n-1}} \left[1 - e^{-\frac{2^{n+1} P_{H_2}^n}{100}} \right] \quad (20)$$

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, it is well to consider the case $n = 3$. Figure 7 shows the partial pressures of atomic hydrogen as calculated from (20) 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.

The experiments in connection with this apparatus depend in the first place on the fact that to an approximation the refractions of two hydrogen atoms is the same as that of a hydrogen molecule. In using the interferometer as a pressure gauge, one need not distinguish between the atoms and molecules but can say that the position of the fringes depends only on the density as in equation (2).

The procedure is to watch the fringes when the two tubes are open to each other and the discharge passes through one of them. The gas leaving one decreases one optical path and since the connecting tube is small, it increases the other. Thus we get a value of the density change from which we could calculate the pressure change and therefore the dissociation if one knew the temperature. Now since the temperature of the outside of the tube was known and since the distribution of temperature could be estimated by the bowing of the fringes the dissociation could be found.

However, it is really necessary to go more deeply into the calculation of the temperature. A complete analysis can be carried out but is by no means a simple matter. Part of the complication is due to the fact that there is ~~an~~ a solid bounded on one side by a fairly conductive low pressure gas which is a

permanent variable source of heat and on the other by a cold gas. The expressions resulting from the geometrical shapes are unwieldy for the juggling around of the curious and unusual boundary conditions which obtain. The whole calculation is of prime importance for a part of the experiment (anomalous dispersion absorption, etc.) which has not yet been carried out and will be reserved until the data is ready. Here only an outline will be drawn to give an idea of the conditions existing.

Since glass is thin walled and is about four times as good a conductor as hydrogen gas, while the air outside is a comparatively poor conductor we may neglect the thickness of the glass and imagine that the hydrogen extended out to r_e the external radius of the glass tube and is there separated from the air by a polished surface.

Again neglecting end effects, Θ the excess temperature over the outside air due to an instantaneous source of heat at time $t = 0$, and of strength $w dt$ is given by the conduction equation

$$\frac{\partial \Theta}{\partial t} = \alpha^2 \left[\frac{\partial^2 \Theta}{\partial r^2} + \frac{1}{r} \frac{\partial \Theta}{\partial r} \right] \quad (21)$$

subject to the conditions

$$\Theta = \Theta_0 = \frac{w dt}{C_h} \quad \text{when } t = 0 \text{ and } r < r_i \quad (22)$$

(23)

where W is the power $d\tau$ is an element of time, C_h is the heat capacity of the hydrogen and h is a constant determined from the steady state (kh is sometimes called emissivity).

The solution of (2)

$$\theta = \sum_j A_j J_0(\mu_j r) e^{-\mu_j^2 \omega^2 t} \quad (24)$$

where $J_0(\mu r)$ is Bessel's function of order zero

where

$$A_j = \frac{2\mu_j^2 \theta_0}{r_e^2 [\mu_j^2 + h^2] J_0(\mu_j r_e)} \int_0^{r_i} r J_0(\mu_j r) dr \quad (25)$$

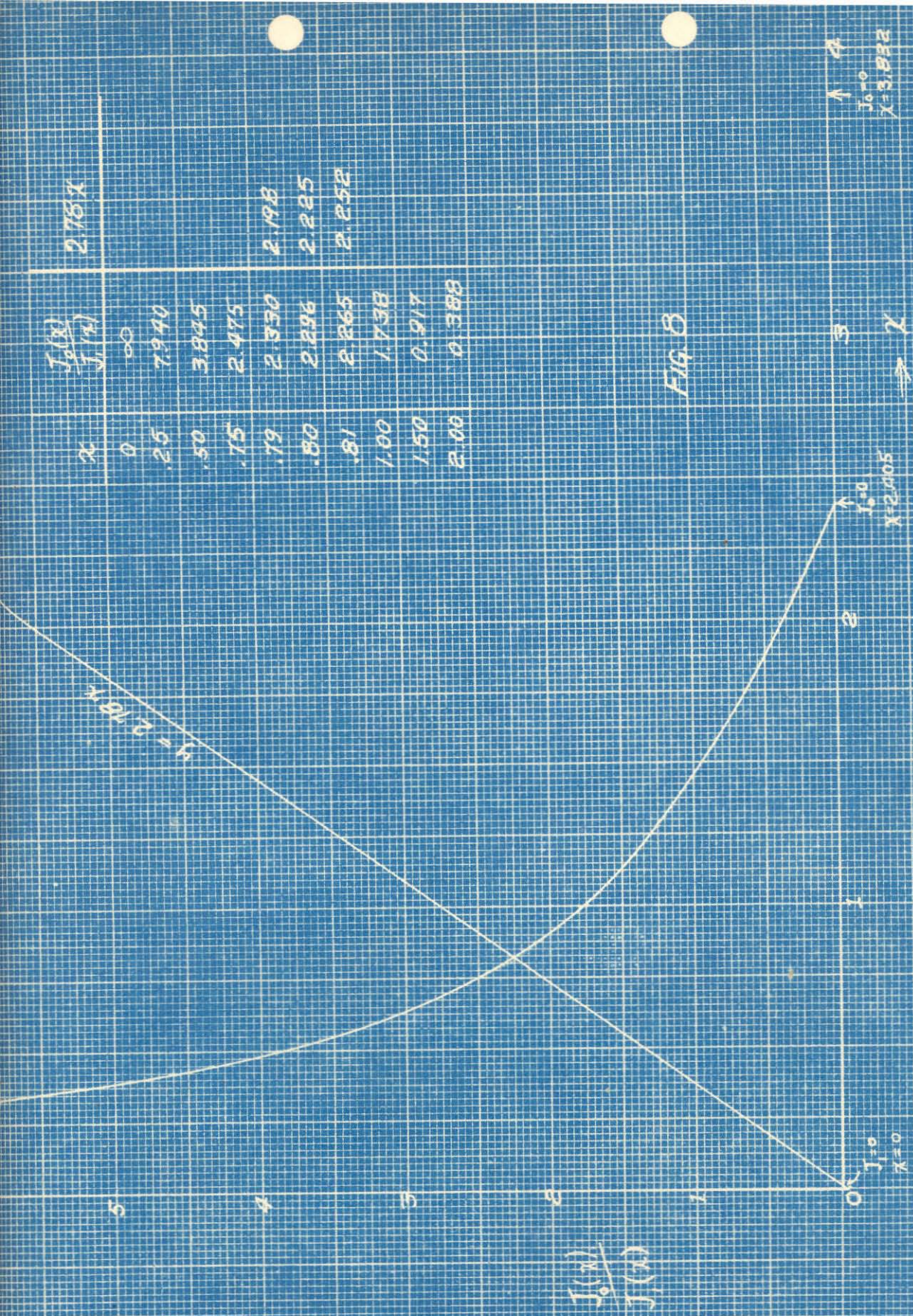
$$= \frac{2h\theta_0}{r_e [\mu_j^2 + h^2] J_0(\mu_j r_e)}$$

and where the μ_j 's are the roots of the transcendental equation

$$\mu J_1(\mu r_e) - h J_0(\mu r_e) = 0 \quad (26)$$

These roots can be found graphically very easily by noticing that

$$\frac{J_0(x)}{J_1(x)} = \frac{x}{r_e h}$$



x	$\frac{J(x)}{J(0)}$	$2.78x$
0	0	
.25	7.940	
.50	3.845	
.75	2.475	
1.00	1.798	2.78
1.50	0.917	4.17
2.00	0.3889	5.56

FIG. 8

$\frac{J(x)}{J(0)}$

$J=0$
 $x=0$

$J=0$
 $x=3.832$

$k = 2.16x$

where $x = \mu r_0$

Plotting $y_1 = \frac{x}{2.4}$ and $y_2 = \frac{J_0(x)}{J_1(x)}$ on the same graph

the intersection satisfies the. This is done in figure 8. Only first root

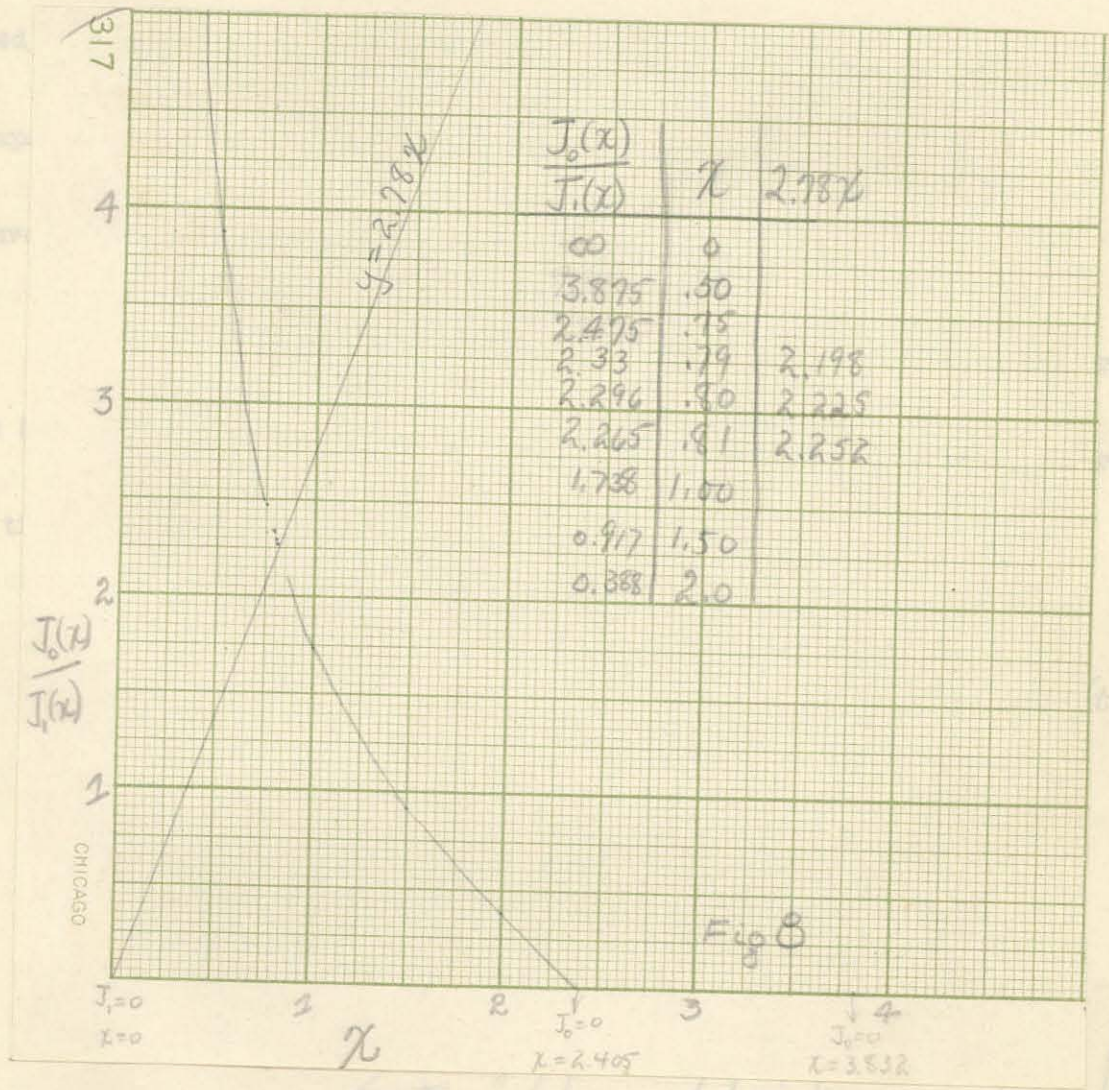


Fig 8

$$a^2 = \frac{k \text{ volume}}{C_h} = \frac{kV}{C_h}$$

$$P(x,t) = \frac{1}{\sum \mu_j} \sum \frac{J_0(\mu_j x)}{\mu_j (J_0^2(\mu_j) + J_1^2(\mu_j))} [1 - e^{-\mu_j^2 a^2 t}]$$

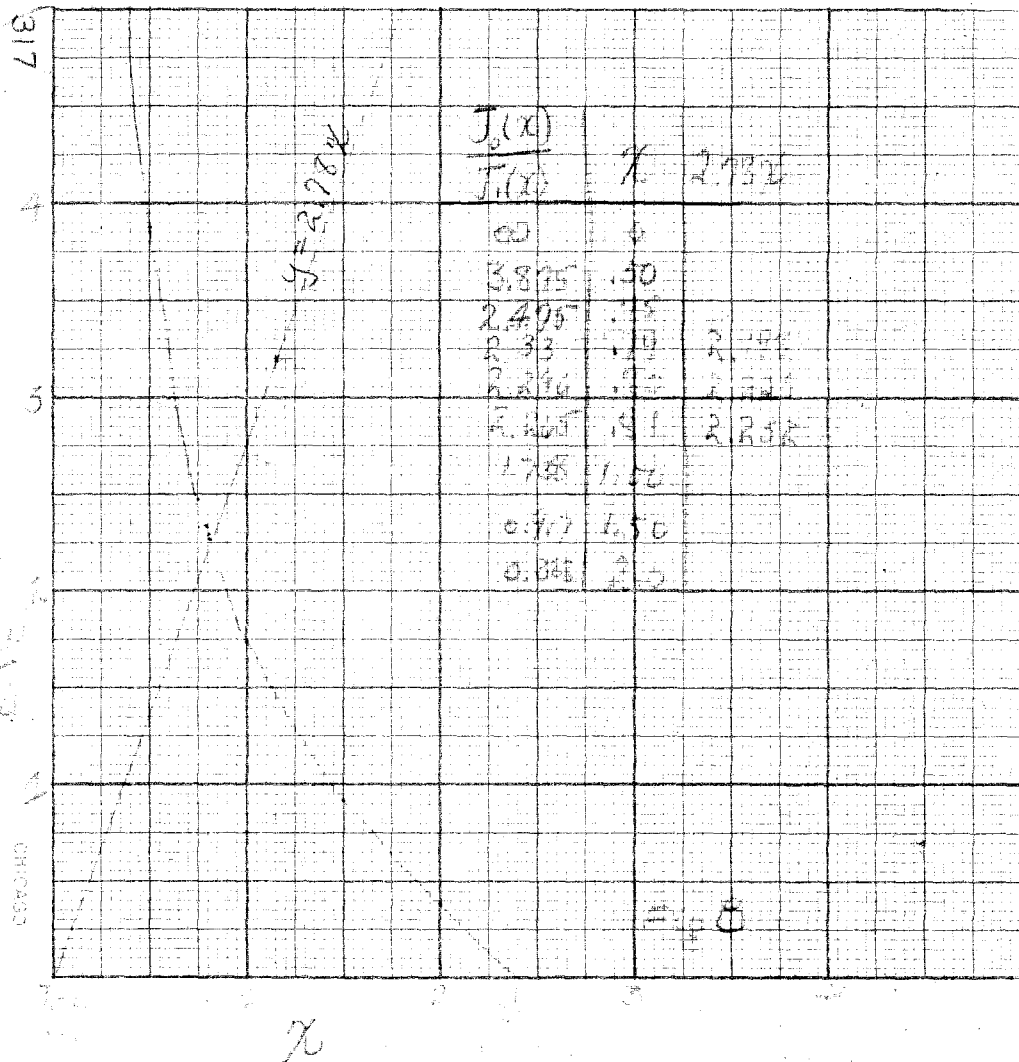


Fig 8

where $x = \mu r_e$

Plotting $y_1 = \frac{x}{r_e h}$ and $y_2 = \frac{J_0(x)}{J_1(x)}$ on the same graph

the intersection satisfies 26. This is done in figure 8. Only first root

need be considered because μ_1 is about four and the final expression for

temperature having $\frac{1}{\mu_j}$ in the denominator of the j^{th} term is so rapidly convergent that only the first term need be considered.

Since the source is a permanent one (and in the experiments the frequency was 500 cycles so that it may be considered constants) the actual temperature at time t after the discharge has been started is

$$\textcircled{H} = \int_0^t \theta(t-\tau) d\tau = \frac{2 h W}{r_e C_h} \sum_j \frac{J_0(\mu_j r)}{(\mu_j^2 + h^2) J_0(\mu_j r_e)} \int_0^t e^{-\mu_j^2 a^2 (t-\tau)} d\tau \quad (27)$$

or

$$\textcircled{H}(rt) = \frac{2 h W}{r_e C_h a^2} \sum_j \frac{J_0(\mu_j r)}{\mu_j^2 (\mu_j^2 + h^2) J_0(\mu_j r_e)} \left[1 - e^{-\mu_j^2 a^2 t} \right]$$

now the diffusivity $a^2 = \frac{k \text{ volume}}{C_h} = \frac{k V}{C_h} \quad (28)$

and we have

$$\textcircled{H}(rt) = \frac{2 h W}{r_e k V} \sum_j \frac{J_0(\mu_j r)}{\mu_j^2 (\mu_j^2 + h^2) J_0(\mu_j r_e)} \left[1 - e^{-\mu_j^2 a^2 t} \right]$$

or by a previous remark

$$\textcircled{H} (r,t) = \frac{2hW}{r_e kV} \frac{J_0(\mu_1 r)}{\mu_1^2 (\mu_1^2 + h^2) J_0(\mu_1 r_e)} [1 - e^{-\mu_1^2 \alpha^2 t}] \quad (29)$$

It turns out that the diffusivity has the enormous value

$$\alpha^2 = \frac{1325}{p}$$

so that the exponential term is negligible and the steady state is reached immediately and as far as the gas is concerned equation (12) applies.

The glass tube has tremendous heat capacity in comparison with the gas and therefore its diffusivity is much lower and the time taken to reach its steady state where the temperature drop across it ~~is~~ small is longer. Because its walls are thin in comparison with its diameter it can be considered as a flat slab and because the gas immediately reaches the steady state the boundary condition inside is that the heat supplied is constant.

A servicable solution for $r_1 < r < r_e$ can be finally obtained from

$$\textcircled{H} (r,t) = \frac{W r}{8\pi r_i L a^2 \sqrt{\pi}} \left[\frac{2a\sqrt{t}}{r} e^{-\frac{r^2}{4a^2 t}} - \sqrt{\pi} + 2 \int_0^{\frac{r}{2a\sqrt{t}}} e^{-\beta^2} d\beta \right] \quad (30)$$

For small values of $\frac{r}{2a\sqrt{t}}$ we can use the uniformly convergent

expansion

$$2 \int_0^{\infty} e^{-x^2} dx = 2 \left(x - \frac{x^3}{113} + \frac{x^5}{215} \dots \right)$$

which gives

$$\Theta = \frac{W r}{8 \pi r_i L a^2 \sqrt{\pi}} \left[\frac{2 a \sqrt{t}}{r} e^{-\frac{r^2}{2 a^2 t}} - \sqrt{\pi} + 2 \left(\frac{r}{2 a \sqrt{t}} - \frac{1}{3} \left(\frac{r}{2 a \sqrt{t}} \right)^3 + \dots \right) \right] \quad (31)$$

For larger values for example $r = r_i + 1$ mm, $t = 25$ sec for which

$\frac{r}{2 a \sqrt{t}} = 1.47$ we can use the asymptotic expansion

$$2 \int_0^{\infty} e^{-x^2} dx = \sqrt{\pi} - \frac{e^{-x^2}}{x} \left(1 - \frac{1}{2x^2} + \frac{1.3}{(2x^2)^2} - \frac{1.3.5}{(2x^2)^3} \dots \right)$$

and get

$$\Theta(r,t) = \frac{W \sqrt{t} e^{-\frac{r^2}{4a^2t}}}{2 \pi r_i L a \sqrt{\pi}} \left[\frac{a \sqrt{t}}{r} - 3 \left(\frac{a \sqrt{t}}{r} \right)^2 + 15 \left(\frac{a \sqrt{t}}{r} \right)^3 \dots \right] \quad (32)$$

The outcome of these calculations is to indicate that at the very start equation (12) may perhaps not be conservative, but after the tube is slightly warm it is alright to use this form in the process of finding the dissociation. This is so because after measuring the expansion one finds the dissociation by first subtracting the part due to temperature change. This part is certainly exaggerated if in the expression about to be derived we use for the lowest

temperature of the gas, the value found by measuring the outside temperature of the glass adding the steady state drop through the walls.

It will be useful in these calculations to introduce \bar{T} the average

temperature in the gas

$$\begin{aligned} \bar{T} &= T_0 - \frac{W}{4\pi r_i^2 kL} \cdot \frac{2\pi}{\pi r_i^2} \int_0^{r_i} r^3 dr \\ &= T_0 - \frac{W}{4\pi kL} \frac{1}{2} = T_0 - \frac{1}{2}(T_0 - T_i) \end{aligned}$$

or

$$T_0 - \bar{T} = \frac{1}{2}(T_0 - T_i) = \frac{W}{8\pi kL} \quad (33)$$

It is \bar{T} which is the effective temperature of the tube in producing the pressure change aside from dissociation, and we see from (33) that it can be calculated directly from W .

To derive the necessary formula we define the dissociation by

$$\gamma = \frac{n_a}{n_{m_1} + n_a} \quad (34)$$

where n_a is the number of atoms in the discharge tube and n_{m_1} the number of molecules.

The total number of molecules n_i in the system is constant and if n_{m_2} is the number of molecules in the cold tube which is at room temperature T and

which contains no atoms, we can write

$$n_0 = n_{m_2} + n_{m_1} + \frac{1}{2} n_a = n_{m_2} + \left(1 - \frac{\gamma}{2}\right) (n_a + n_{m_1}) \quad (35)$$

If v_1 , and v_2 are the volumes of the discharge tube and the cold tube respectively, and if p_0 is the initial pressure and p the final pressure which is constant throughout the system, we can write the gas law

$$pv_1 = (n_{m_1} + n_a) R \bar{T}$$

$$pv_2 = n_{m_2} R T \quad (36)$$

$$p_0(v_1 + v_2) = n_0 R T$$

Substituting from (35) and solving for γ

$$\gamma = \frac{2\bar{T}}{pv_1} \left(\frac{pv_1}{\bar{T}} + \frac{pv_2}{T} - \frac{p_0(v_1+v_2)}{T} \right)$$

or

$$\gamma = 2 \left[1 + \frac{\bar{T}}{T} \left(\frac{v_2}{v_1} \frac{\Delta P}{P} - \frac{P_0}{P} \right) \right] \quad (37)$$

By an elementary calculation using (N is the fringe-shift if one tube were pumped out) $\frac{\Delta N}{N} = \frac{2\Delta P}{P}$ and also equation (4) with all numerical values in it.

$$\gamma = 2 \left[1 - \left(\frac{1.028P - \Delta N}{1.028P + \Delta N} \right) \frac{\bar{T}}{T} \right] \quad (38)$$

It might as well be pointed out here that when the dark space gauge was used (37) served to calculate γ but since the volume of the gauge was entirely negligible this becomes

$$\gamma = 2 \left[1 - \frac{\bar{T}}{T} \frac{P_0}{P} \right] \quad (39)$$

or more conveniently

$$\gamma = 2 \left[\frac{\Delta P}{P} - \frac{\Delta T}{T} \left(1 + \frac{\gamma}{2} + \frac{\gamma^2}{4} + \dots \right) \right] \quad (40)$$

The pressure changes in the gauge were calculated from the well known

law in which the dark space d is given by

$$d = \frac{.26}{P} + \frac{.43}{\sqrt{i}} \quad \text{for hydrogen} \quad (41)$$

and

$$d = \frac{.36}{P} + \frac{.49}{\sqrt{i}} \quad \text{for helium} \quad (42)$$

with the voltage kept constant.

In these expressions the second term depending on current density can be neglected for our purposes.

The data calculated from equations (38) on, show that the dissociation depends on the condition of the tube and slightly on the frequency and the power.

The values at the pressures used ranging from 0.5 to 2 mm (usually above 1 mm) reached twenty to thirty percent using the gauge data and somewhat more when the interferometer method or the helium check method was used. These values are in good agreement with the estimates from Bonhoeffer's data. The measures are unfortunate in involving big corrections for small effects. Worst of all is the uncertainty of the value of W the power. This apparently simple quantity is hard to get at. The wattmeter readings which were actually used do not represent the energy dissipated in the tube. Energy escapes at the electrodes in no inconsiderable amount. More important are the losses in the transformer and the condensers as well as the high voltage voltmeter and other parts of the circuit. The first two may account for 20% of the power and the voltmeter might sometimes have required 150 to 250 watts. Such losses if they could be corrected for might show double the values of the dissociation. For high powers the error might be very large. For example take equation (40) for small and high power such that $\frac{\Delta P}{P}$ might be .4. Suppose that $\frac{\Delta T}{T}$ calculated from W to which it was closely proportional was also .4 so that $\gamma = 0$. If not the trivial correction of 5% for radiation is made of W , the value of γ becomes 4%, if 20% is allowed for condenser loss $\gamma = 20\%$. If 25% is attributed to voltmeter loss $\gamma = 40\%$.

It is seen that this work must be carried further.

D. ESTIMATE OF ERROR. Let us not insist on the possible high values of γ

and be satisfied to say that $\frac{n_a}{n_a + n_m} = \gamma$ was at least 0.25 at original pressure

2mm, that the shift was no more than 0.03 fringes and that accidental errors

were absent. Substituting all values into equation (4) we have partial

pressure of atomic hydrogen is $0.25(1 + 0.25)p$

$$\pm 0.03 = \frac{0.25 \cdot 90}{6 \times 10^{-5}} \cdot \frac{273}{293} \frac{1.25P}{760} \left[2(\mu_H^{-1}) - (\mu_{H_2}^{-1}) \right]$$

or

$$2(\mu_H^{-1}) = \mu_H^2 - 1 = + \frac{0.03 \cdot 6 \times 10^{-5} \cdot 293 \cdot 760}{0.25 \cdot 90 \cdot 273 \cdot 2(1.25)} + \frac{(\mu_{H_2}^{-1})}{1}$$

$$= \left[1.38 \pm .26 \right] \times 10^{-4} \quad (43)$$

This is the figure that is to be compared with the theory. Apparently there is a bad discrepancy. The theoretical $(\mu_H^2 - 1)$ calculated for example from the second order Stark effect term as derived by Epstein and others gives

$$(\mu_H^2 - 1) = 2.3 \times 10^{-4}$$

The order of the discrepancy can be judged by using the theoretical value to calculate the expected fringe shift at 2 mm using measured atomic

hydrogen concentration.

Substituting in equation (4)

$$\Delta N = \frac{.25 \cdot 90 \cdot 273 \cdot 1.25 \cdot 2}{6 \times 10^{-5} \cdot 293 \cdot 760} \left(2.3 \times 10^{-4} - 1.38 \times 10^{-4} \right)$$

we get

$$\Delta N = .11 \text{ fringes}$$

A shift which would have been plainly visible in every observation, even under bad conditions.

Another point of view is to say that if the shift was less than 0.03 fringes, there must have been less than 8% atomic hydrogen in the best case. This is out of the question. The estimates of 25% are conservative, for the tube in which the fringe shift was measured was in the best of condition and equalled tubes in which other observers claim 100% dissociation.

In such a state of affairs it behoves us to examine closely the theory underlying the predictions which are tested by the experiment.

THEORY OF THE NORMAL HYDROGEN ATOM.

Schrodinger's wave equation for this case

$$\Delta \Psi + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r} \right) \Psi = 0 \quad (44)$$

has been well investigated, and the solutions satisfying the necessary conditions are known to have the form

$$\Psi_{lmm} = \chi_{lm}(r) Y_m^l(\theta, \varphi) e^{\frac{2\pi i E t}{h}} \quad (45)$$

The Y_m^l are spherical harmonics and since we are dealing with normal

hydrogen we may disregard them because of the restriction that $\Delta n = \pm 1$

and because the electric moment induced by a light wave is parallel to it,

so that $\Delta m = 0$. Since n is zero for the normal state the only functions

that appear are Y_0^0 and Y_1^0 which are constant and we may confine our atten-

tion to the functions $\chi_{lm}(r)$. Explicit formulae are available for this

function but as is so often the case, we find it most convenient for actual

numerical calculation to derive the value of Ψ directly from the fundamental

integrals which arise in the method of Laplace, namely

$$\chi_{lm}(r) = r^n \int_0^{\infty} e^{-zr} \left(z - \frac{4\pi^2 m e^2}{h^2 l} \right)^{l+m} \left(z + \frac{4\pi^2 m e^2}{h^2 l} \right)^{n-l} dz \quad (46)$$

where C is a contour which has to satisfy a condition, a sufficient but not necessary form of which is

$$\int_C \frac{dz}{z} \left[e^{-z} \left(z - \frac{4\pi^2 m e^2}{h^2 l} \right)^{l+n+1} \left(z + \frac{4\pi^2 m e^2}{h^2 l} \right)^{n-l+1} \right] dz = 0 \quad (47)$$

For negative values of E in (44), l must be an integer and (47) is

satisfied by choosing a closed path around the only pole $z = -\frac{4\pi^2 m e^2}{h^2 l}$

For positive E, l need not be an integer and to get the whole transcendental a more complicated path is required and one must be satisfied with an approximate solution. The main difficulty is to get the normalizing function and this can be found from the work of Oppenheimer.

Knowing all about ψ we can go on and inquire about the distribution in space and time of electric charge density. This is given according to Schrodinger by

$$\rho = \psi \bar{\psi} \quad (48)$$

If we denote by ψ the properly normalized part of (44) which does not depend on the time, the charge density in an isolated hydrogen atom in the normal state $l = 1, m = n = 0$, subjected to the action of a light wave

$$F \cos 2\pi \nu t$$

$$\psi \bar{\psi} = u_1^2(r) - 2 F e \cos 2\pi \nu t \left[\sum_{l=1}^{\infty} \frac{(E_1 - E_l) a_{1l} u_1(r) u_l(r)}{(E_1 - E_l)^2 - h^2 \nu^2} + \int_0^{\infty} \frac{(E_1 - \mathcal{E}) \alpha_1(\mathcal{E}) u_1(r) u(\mathcal{E}, r)}{(E_1 - \mathcal{E})^2 - h^2 \nu^2} d\mathcal{E} \right] \quad (49)$$

where

$$a_{1l} = \int_0^{\infty} \int_0^{\pi} (r \cos \theta) r^2 \sin \theta \cdot u_1(r) u_l(r) d\theta dr \quad (50)$$

and

$$\alpha_1(\mathcal{E}) = \int_0^{\infty} \int_0^{\pi} r \cos \theta \cdot r^2 \sin \theta u_1(r) u(\mathcal{E}, r) d\theta dr \quad (51)$$

From this point the Schrodinger method is to follow accurately the classical theory in which the electric moment is

$$M_x = \int p_x d v$$

and the index of refraction is given by

$$\mu^2 - 1 = \frac{4\pi N M(t)}{F \cos 2\pi \nu t} \quad (52)$$

Where $M(t)$ is the variable part of the electric moment and N the number of particles per cm^3 .

Applying these to (49) there results finally

$$(\mu^2 - 1) = 2\pi N \left[\sum_1^{\infty} \frac{(E_l - E_1) a_{1l}^2}{(E_1 - E_l)^2 - h^2 \nu^2} + \int_0^{\infty} \frac{(E - E_1) \alpha_1^2(E)}{(E_1 - E)^2 - h^2 \nu^2} dE \right] \quad (53)$$

This equation is identical in form with the classical expression for a set of oscillators with natural frequencies $(E_1 - E_l)$ and also a set with continuously varying frequencies $(E - E_1)$. The numerical values for the first three terms of the summation and for the contribution of the continuous spectrum are given in order for the case of the hydrogen atom in the normal state undisturbed by outside forces.

$$(\mu_H^2 - 1) = 1.52 \times 10^{-4} + 0.28 \times 10^{-4} + 0.06 \times 10^{-4} + 0.21 \times 10^{-4}$$

The sum which is still low, is already greatly in excess of our experimental value. But we have imagined that the atom is alone, while as a matter of fact it is in a gas at pressure, let us say, around 2 mm.

Now if we say that (49) literally described the distribution of charge in space, we see that under the action of the light the normal hydrogen atom which originally (figure) was a spherically symmetrical distribution of charge decreasing in density exponentially with r is greatly expanded and the hydrogen electron is spread partly in large shells as shown in figure .

These shells correspond to excited states of hydrogen. They are important in the dispersion because of their large moments. On the other hand the change that another atom will approach to a given radius depends on the square of that radius so that these higher states will suffer many more collisions than the lowest state. Foote has shown that whenever a collision may affect a quantum state it does. In other words collisions of the second kind have 100% efficiency.

Calculating the number of collisions on the basis of kinetic theory it turns out that all the higher states are completely destroyed in the time taken for the passage of one wave train and their contribution to coherent scattering lost and so should not be added in to the electric moment. This makes $\mu_{H}^2 - 1$ equal to 15.8 or less since there is some loss from the lowest term. In any case the results are now equal to the experimental value within the estimated error.

CONCLUSIONS.

The experiment is therefore not in disaccord with the theory but actually offers evidence that the theory is literally true. The excited hydrogen atom is apparently really a shell of electricity and in general the quantity ϕ describes the space occupied by an atom in the kinetic theory sense, and once more we have a concrete model of the structure of matter.

Moreover it is to be expected that the destruction of excited states takes place in all atoms and that therefore the refractivity will depend on pressure and deviate from equation (2). Pressure effects have been looked for, but always at high pressures, while this one is probably over above pressures of one mm. It is hoped that an opportunity will be had to search for this change at very low pressures. It may give important evidence on the excited states of atoms and molecules.

The author realizes that any virtue in this work is largely due to his privilege of starting, planning and almost completing it at the Norman Bridge Laboratory in Pasadena, California. The problem was first brought to his notice by Prof. St. Loria and engaged his interest because of some theoretical considerations by Prof. P.S. Epstein. The deep intuitive insight of Prof. R. A. Millikan

played a guiding role throughout the work and furnished besides strict criticism in particular places.

The author is proud to attribute his knowledge of experimental technique to association with his colleagues at the California Institute of Technology, especially I.S.Bowen, W.R.Smythe, A.L.Klein, R. Kennedy, Sinclair Smith, C.B.Millikan, W.V.Houston, O.Oldenbergh, C.Eckart, E.C.White, and others who were always willing to discuss difficulties and always able to offer valuable suggestions for surmounting them.

Thanks is due to the Naval Research Laboratory, and especially to Dr. E. O. Hulburt for permission to continue the work there and for providing many usual facilities for its prosecution.