Spectroscopic Determination of the Rydberg Constants and the Value of e/m from H-alpha and D-alpha

Thesis

by

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Summary

The wavelengths of the H-alpha and D-alpha lines were measured with a Fabry-Perot interferometer directly against the primary standard of wavelength, 6438.4696 I.A. A Michelson lamp was constructed to provide a light source for the red cadmium line, and a Geissler-Wood discharge tube was designed to emit the H-alpha and the D-alpha. To increase the sharpness of the lines, the tube was cooled in liquid air under low pressure. In order to avoid errors due to slight environmental changes, each of the lines was photographed simultaneously with the standard line on the same spectroscopic plate. The results of the measurements are : 6562.85337 ± 0.00022 I.A. for H-alpha, and 6561.06811 ± 0.00005 I.A. for D-alpha.

From the above values for the respective wavelengths, the Rydberg constants for hydrogen R_H , for deuterium R_D , for helium R_{He} , and for infinite mass R_∞ , and also the value of e/m and E, the atomic weight of electron, were calculated. They are listed below :

$R_H = 109,677.5795 \pm 0.0037 \quad cm^{-1}$,

$R_D = 109,707.4226 \pm 0.0008 \quad cm^{-1}$,

$R_{He} = 109,722.2694 \pm 0.0024 \quad cm^{-1}$,

$R_\infty = 109,737.3111 \pm 0.0041 \quad cm^{-1}$,

$e/m = (1.75883 \pm 0.00022) \times 10^7$ e.m.u./gm.,

* $E = (5.48740 \pm 0.00069) \times 10^{-4}$.

The intensity ratio for H-alpha and for D-alpha was found to be 0.808 ± 0.004 and 0.803 ± 0.003, respectively, as compared to the theoretical value of 0.806 .

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* $1/E = 1822.36 \pm 0.23$, number of electrons per unit atomic weight ;
$H/E = 1837.17 \pm 0.24$, ratio of mass of hydrogen atom to that of electron .

Contents

1. INTRODUCTION

Prior to 1941, the accepted values of the Rydberg constants were based solely on Houston's data of 1927[1]. By means of a Fabry-Perot interferometer he measured the wavelengths of the hydrogen lines, 6563 A and 4861 A, and of the helium line, 4686 A, with reference to the helium line 5051 A as the standard, the wavelength of which was assumed to be 5051.6750 I.A. Although his work was very important and precise his values were subject to an uncertainty because he did not use the primary standard, the red cadmium line 6438.4696 I.A., for the reference.

In 1939, Drinkwater, Richardson and Williams (D.R.W.)[2] made further determinations of the Rydberg constants with a reflection echelon of 40 plates. They measured in vacuum the wavelengths of the hydrogen line, H-alpha, and the deuterium line, D-alpha, with reference to the standard cadmium line emitted from an Osira cadmium lamp. Later, Birge adopted the values of the Rydberg constants exclusively on the basis of their work[3]. The results obtained with a Fabry-Perot interferometer were omitted.

Since the Rydberg constants, R_H and R_∞, and e/m are very important atomic constants, every different method of high precision should be used for the determination of their values. Many

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[1] W. V. Houston, Phys. Rev. 30, 608 (1927).
[2] Drinkwater, Richardson and Williams, Proc. Roy. Soc. A174, 164 (1940).
[3] R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).

physicists and physical chemists think without hesitation that the Rydberg constants are well determined. However, according to Birge[4] and Stille[5], the values of the Rydberg constant for hydrogen and deuterium have not been measured with a Fabry-Perot interferometer, referring directly to the cadmium primary standard of wavelength. Although reflection echelon may have some advantages, the Fabry-Perot interferometer can yield as great an accuracy and is most widely used for precise wavelength measurement in the visible region of the spectrum. Therefore, further measurements of the H-alpha and D-alpha lines with the latter instrument are highly desirable.

To provide the primary standard of wavelength, a light source for the red cadmium line was constructed in this laboratory[6] in accordance with the specifications adopted by the International Conference for Weights and Measures in 1935 and by the International Astronomical Union in 1938. It should produce the standard wavelength exactly. This light source has made it possible to photograph simultaneously the line H-alpha, or D-alpha, with the red cadmium line on the same spectroscopic plate and thus to measure their wavelengths by direct comparison with the primary standard.

The reflection echelon used by D.R.W. had a fixed plate

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4. R. T. Birge, Phys. Rev. 60, 766 (1941).
5. U. Stille, Zeit. f. Phys. 121, 133 (1943).
6. C. W. Hsueh, Phys. Rev. 65, 151 (1944).

thickness of 6.88 mm. which corresponded to only one separation of the Fabry-Perot interferometer. In the case of an interferometer, several different gaps between the two plates can be used and an average can thereby be obtained from the observations with an instrument which can have as high a resolving power as a reflection echelon and can still be operated as several echelons of different plate thicknesses. In addition, experiments have been done to cool a hydrogen discharge tube with rapidly evaporating liquid air[7]. Temperatures as low as 56°K was reached. Theoretically, this method of cooling could make the hydrogen and the deuterium lines sixteen per cent narrower than the conventional method. The microphotometer curves showed that the two main components of the H-alpha line could be clearly separated and that the third component of the D-alpha line could be revealed. Consequently, work was undertaken to determine the Rydberg constants by using the Fabry-Perot interferometer and the primary standard of wavelength, in conjunction with a light source for the H-alpha and D-alpha lines, cooled with liquid air under low pressure.

At first sight, it may seem a disadvantage that our Fabry-Perot interferometer spectrograms were taken in air, not in vacuum. The disagreement among the various determinations of the refractive index and the dispersion of air may introduce some error in our

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7. C. W. Hsueh, Phys. Rev. 62, 303 (1942) ; Rev. Sci. Inst. 14, 250 (1943).

final values of R and of e/m. Nevertheless, the accepted primary standard of wavelength at the present time is the air wavelength of the red cadmium line. Although D.R.W. placed their echelon in vacuum and thus avoided some difficulties in connection with the refractive index and the dispersion of air, they had to use the refractive index of air to convert the accepted value of wavelength standard, 6438.4696, to a corresponding value in vacuum. On this converted standard their measurements were founded. In our work, we first obtained the wavelength values of H-alpha and D-alpha in direct reference to the adopted primary standard and then converted the air wavelength thus obtained to the corresponding values in vacuum to get the wave numbers. Furthermore, the lines, H-alpha and D-alpha which we measured, and the standard line are in the same spectral region and so close together that the corrections for the dispersion of air are less than 0.0001 A and can be safely neglected. Hence, as long as the air wavelength of the red cadmium line remains the primary standard of wavelength, both the results of D.R.W. and those obtained in this work should be exposed to the same degree of error due to any uncertainty of the refractive index of the normal air.

2. THE STANDARD OF WAVELENGTH

The value of the wavelength of the red cadmium line, 6438.4696 I.A., has been adopted as the primary standard of wavelength by the International Astronomical Union[6] and by the International Conference for Weights and Measures[7]. At present, the best available commercial light source for the standard cadmium line is the Osira cadmium lamp, sold by Adam Hilger, Ltd. of England. Using a Fabry-Perot interferometer, Jackson[8] found that the wavelength of the standard line emitted by the Osira lamp with an exciting current not exceeding 1 ampere agreed with that given by the Michelson lamp within 0.0001 A. It appeared, then, that the Osira lamp could be used as a reliable substitute for the latter. Other considerations, however, led us to relinquish the use of commercial light sources. In the first place, the intensity of the red cadmium line from the Osira lamp was rather low for our purpose. It usually took six hours' exposure of only the cadmium line to get an interferometer spectrogram. Besides, the Osira lamp, like most electric lamps, has a limited life of only 100 to 200 hours, and was not replaceable on account of the War. The other commercial cadmium lamps, which we could get, gave a red cadmium line too broad for precise work,

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[6] Tran. I.A.U. 2, 47, 232 (1925).; Ibid, 6, 79 (1939).
[7] Procès-Verbaux Comité Int. Poids et Mésures [2] 17, 91 (1935).
[8] C. V. Jackson, Proc. Roy. Soc. A155, 407 (1936).

and could not reproduce the standard wavelength exactly.

In order to provide a satisfactory source for the red cadmium line, a Michelson lamp was constructed in our laboratory. The specifications of the International Astronomical Union and of the International Conference for Weights and Measures were closely followed so that the standard wavelength could be reproduced exactly. The lamp consisted essentially of a discharge tube in an electric furnace maintained at a temperature between 300°C and 320°C. The discharge tube had two pyrex glass bulbs joined together by a U-shaped capillary, 9 cm. in length and 2.5 mm. in diameter. Each bulb had a diameter of 2.7 cm. and a length of 6 cm. A diagram of the tube is shown in Fig. 1. In each of the two bulbs was mounted a copper electrode. These electrodes, due to the copper oxide formed on the surface, had some advantage of absorbing the undesirable hydrogen gas, which was formed from the decomposition of water vapor or grease at low pressure. The tube was excited by a 1-kva Thordarson wireless transformer which furnished a secondary voltage from 4 to 25 kilovolts. An auto-transformer was used to supply the primary voltage of the exciting transformer, which run from 15 to 140 volts. By controlling the current, the tube was protected from overheating by means of three 9000-ohm resistors, which were connected to the transformer in

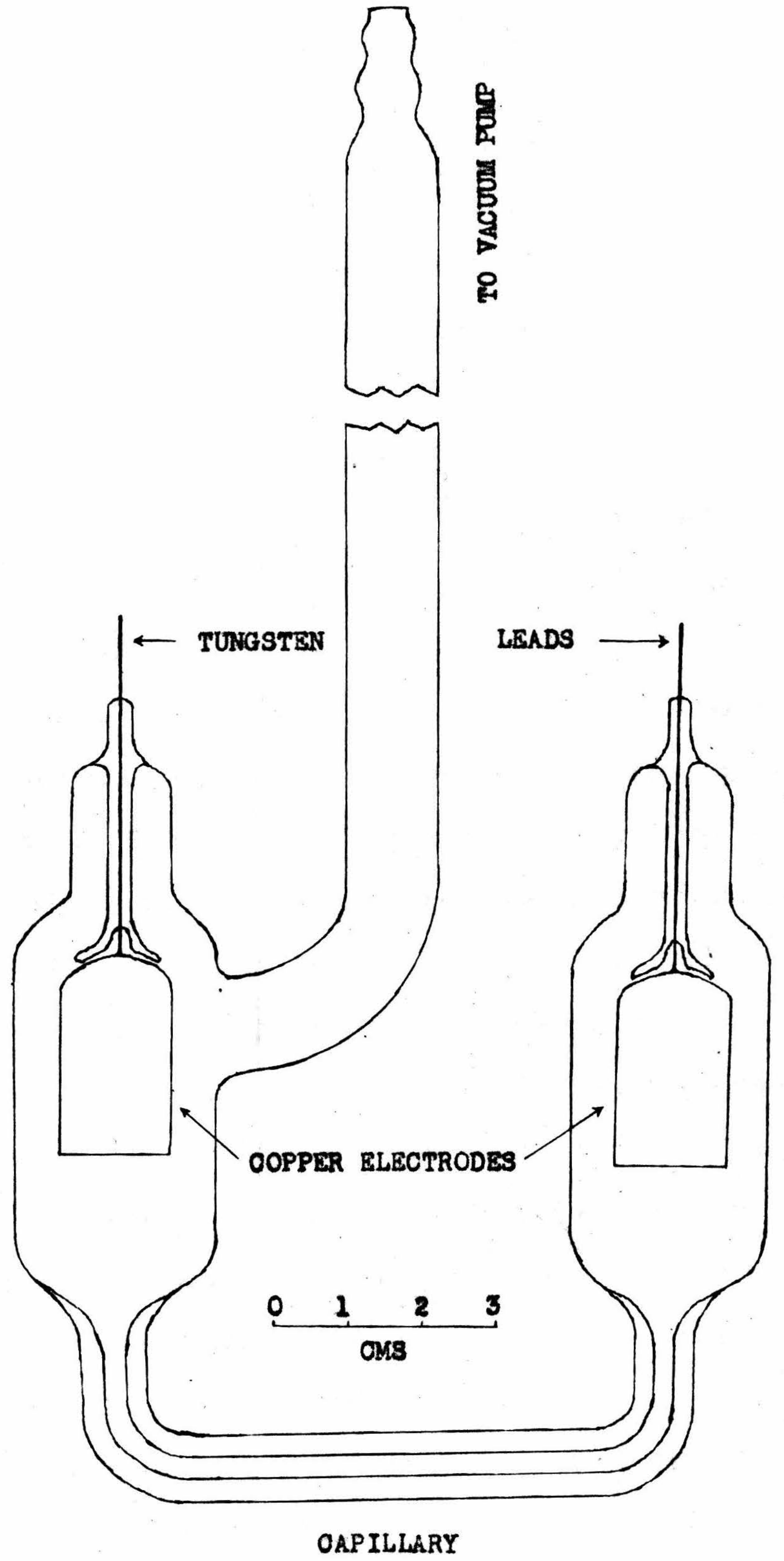

Fig. 1. The cadmium discharge tube

series with the tube. Jackson[8] carefully compared the wavelengths of the red cadmium line given by the Michelson lamp carrying currents of 5, 10 and 20 mA, respectively, and found no measurable difference in the wavelength. Accordingly, our lamp was run with exciting currents always below 20 milliamperes.

The Michelson tube contained about 150 milligrams of pure cadmium metal distributed in its two bulbs. In order to vaporize the metal and maintain the cadmium discharge, the tube was heated in an electric furnace, a diagram of which is shown in Fig. 2. A terra-cotta thimble, 6 inches long, 11/16 inch thick and 5 inches in diameter, was used for the core of the furnace, around which twenty turns of No. 20 (B and S gauge) chromel wire were wound. The thimble was actually a coarse porcelain cylinder generally used in chimneys. To eliminate the magnetic field of the heating current, which might produce the Zeeman-effect broadening of the standard line, ten turns wound clockwise and ten turns wound counter-clockwise were juxtaposed. The windings were fixed to the thimble by means of "Insalute" adhesive cement, which is a nonconductor and can withstand a high temperature. The heating core of the furnace was suspended on a frame of asbestos boards held together with four threaded steel rods, and surrounded by a thick layer of diatomaceous earth for heat insulation. The

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[8] C. V. Jackson, Proc. Roy. Soc. A<u>155</u>, 407 (1936).

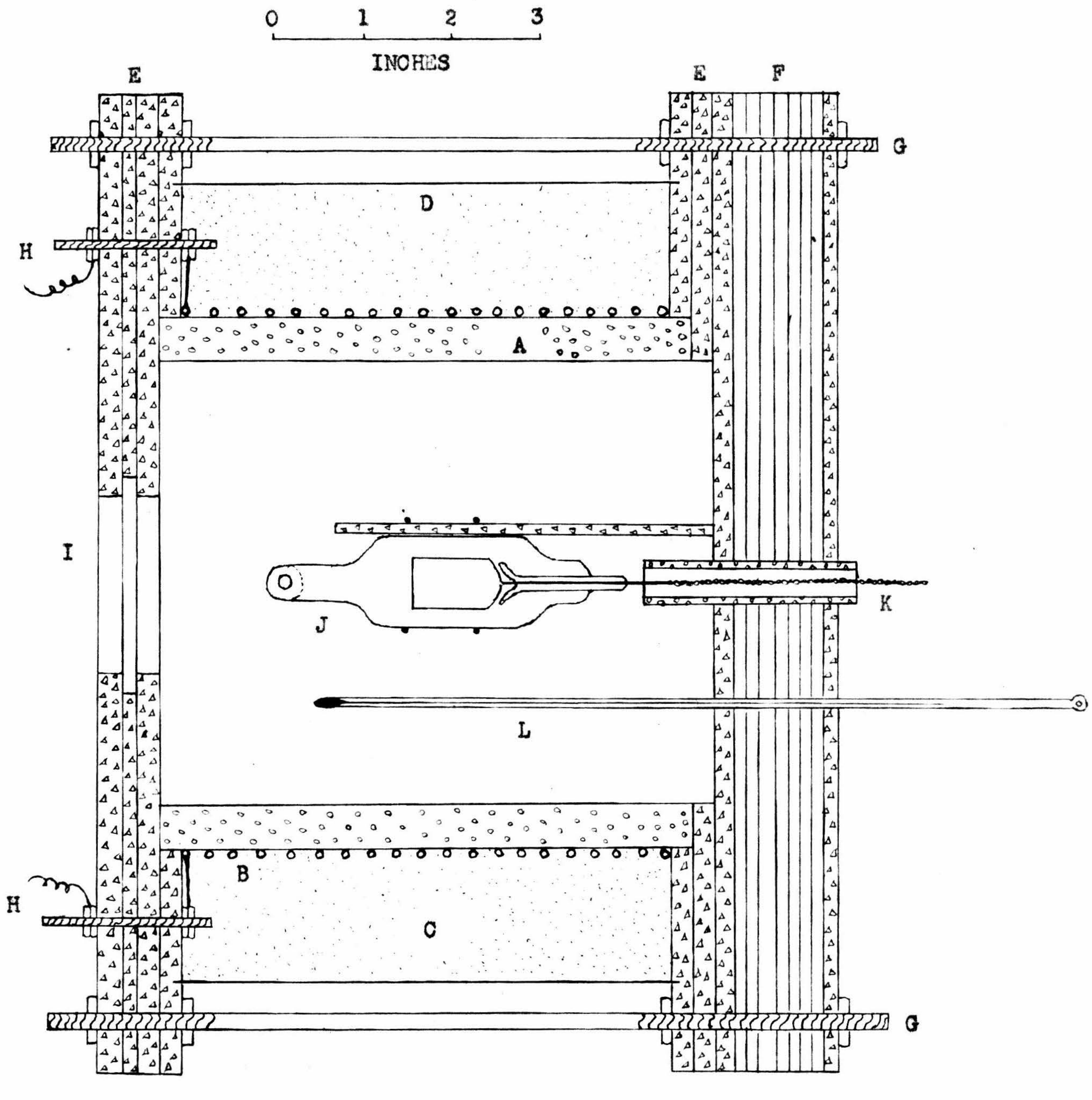

Fig. Electric furnace for the cadmium discharge tube

A - terra-cotta thimble ; B - heating coil ; C - diatomaceous earth ; D - sheet-metal cylinder ; E - asbestos boards ; F - asbestos sheets ; G - threaded steel rods ; H - leads for heating current ; I - Pyrex glass window ; J - cadmium discharge tube ; K - porcelain insulating pipe and lead to transformer ; L - thermometer, 0° to 360°C.

discharge tube was placed inside the thimble which was equipped with a front window of pyrex glass, 6 cm. wide by 7 cm. long. As the exciting voltage of the cadmium discharge was rather high, sufficient electric insulation was necessary. Hence, the connections of the discharge tube to the transformer were insulated with porcelain pipes, and the tube itself was fastened to an asbestos boatd with fiber-glass cordage, or asbestos string, both of which are good insulators and heat resistant.

In using the Michelson lamp, the tube was evacuated with a good hyvac pump and then closed. The furnace was started with a heating current of about 5 amperes and subsequently maintained at a temperature around 310°C. with a current of about 2.5 amperes. When the tube was newly filled with cadmium metal the appearance of the red cadmium line was often very slow. Another experimental inconvenience was the appearance of the hydrogen line, H-alpha, in the spectrum of the Michelson lamp, owing to the atomic hydrogen which arose from the decomposition of grease or water vapor at low pressures. These two disagreeable factors were eliminated by flushing the tube with oxygen gas, or air, while the tube was lukewarm, and then pumping it to a low pressure. Thereupon, the red cadmium line appeared almost immediately after the furnace was heated up, and the H-alpha line disappeared. Only one flushing with oxygen was needed for each refill of the cadmium metal. Sometimes, the discharge in the capillary consisted of striations and the spectrograph slit could not be uniformly illuminated. This was due to the fact that the pressure inside the tube was rather high. To remove such striations, the furnace was cooled down to around 250°C and the tube was further evacuated until an excitation of 10 kilovolts could not produce any discharge. Then a bright and even discharge was obtained when the tube was heated up again to about 310°C.

In designing the Michelson lamp, precautions were taken to eliminate the objections raised against the lamp of the form originally used by Michelson[9]. The chief objections were : (1) The intensity of the standard line was relatively low ; (2) The capillary discharge viewed end-on was not an extended source and did not permit the illumination of a long spectrograph slit ; (3) The high temperature of the discharge tube added an undesirable Doppler-effect broadening to the line.

In our lamp the intensity was increased by using a capillary of small bore (2.5 mm. diameter) to concentrate the light. The electrodes took the form of a circular cup with an opening of 1.5 cm. in diameter, which was amply large to cover the capillary bore. Thus, the intensity of the standard line was made very strong.

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[9] A. A. Michelson, Light waves and Their Uses (The University of Chicago Press, Chicago, 1907), first edition, pp. 75-76.

Although the intensity of the red cadmium line was reduced to one half by the half-silvered mirror used for the simultaneous exposure with the H-alpha line, a satisfactory grating-interferometer spectrogram could be produced with only 30 minutes' exposure or less.

Michelson used his cadmium lamp with the capillary discharge viewed from one end. Only an area equal to the cross-section of the capillary was used for illumination. As a result, the light-source was not an extended one, and it was very difficult to illuminate a long spectrograph slit evenly with such a small circular source. In our lamp, a photograph of which appear in Fig. 3, the capillary discharge, a white vertical line in the center of the picture, was viewed from one side. All the effective light-emitting area of the capillary discharge, 50 cm. long by 2.5 mm. wide, could be used for illumination. It was large enough to cover most spectrograph slits. However, the light source could be enlarged further to twice its area, or more, by using a magnifying lens.

When Michelson studied the red cadmium line, the light was observed in a direction parallel to that of the current. In this way, the motion of the illumination atoms, the velocities of which increase with temperature, usually contributes an undesirable Doppler-effect broadening to the line. In our lamp the light was

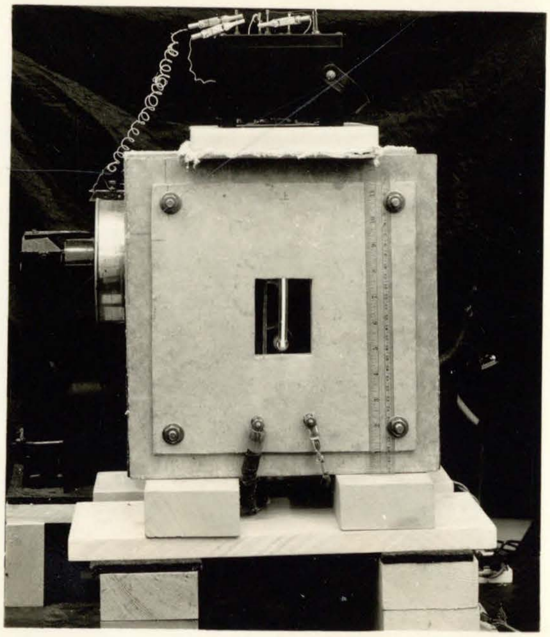

Fig. 3. Photograph of the light source for the standard cadmium line.

observed in a direction perpendicular to that of the current. The motion of the illuminating atoms should produce no, or very little, Doppler effect. Furthermore, Michelson used two rings for electrodes, between which was the capillary. In his lamp the electric field around the capillary was large, especially when a high voltage of 10 kilovolts or more was used to excite the tube. The electrodes in our lamp were situated on one side of the capillary and, therefore, the electric field aroud the capillary should be small. For this reason, the Stark-effect broadening, if there was any, should be small in our case.

Interferometer spectrograms of our lamp were compared with spectrograms of the Osira cadmium lamp by means of a magnifier. For spectrograms of about the same blackness, our standard line was found to be as sharp as, or even sharper than, the standard line of the Osira lamp. An interferometer pattern of the standard line of the cadmium lamp used in this work is shown in Fig. 4.

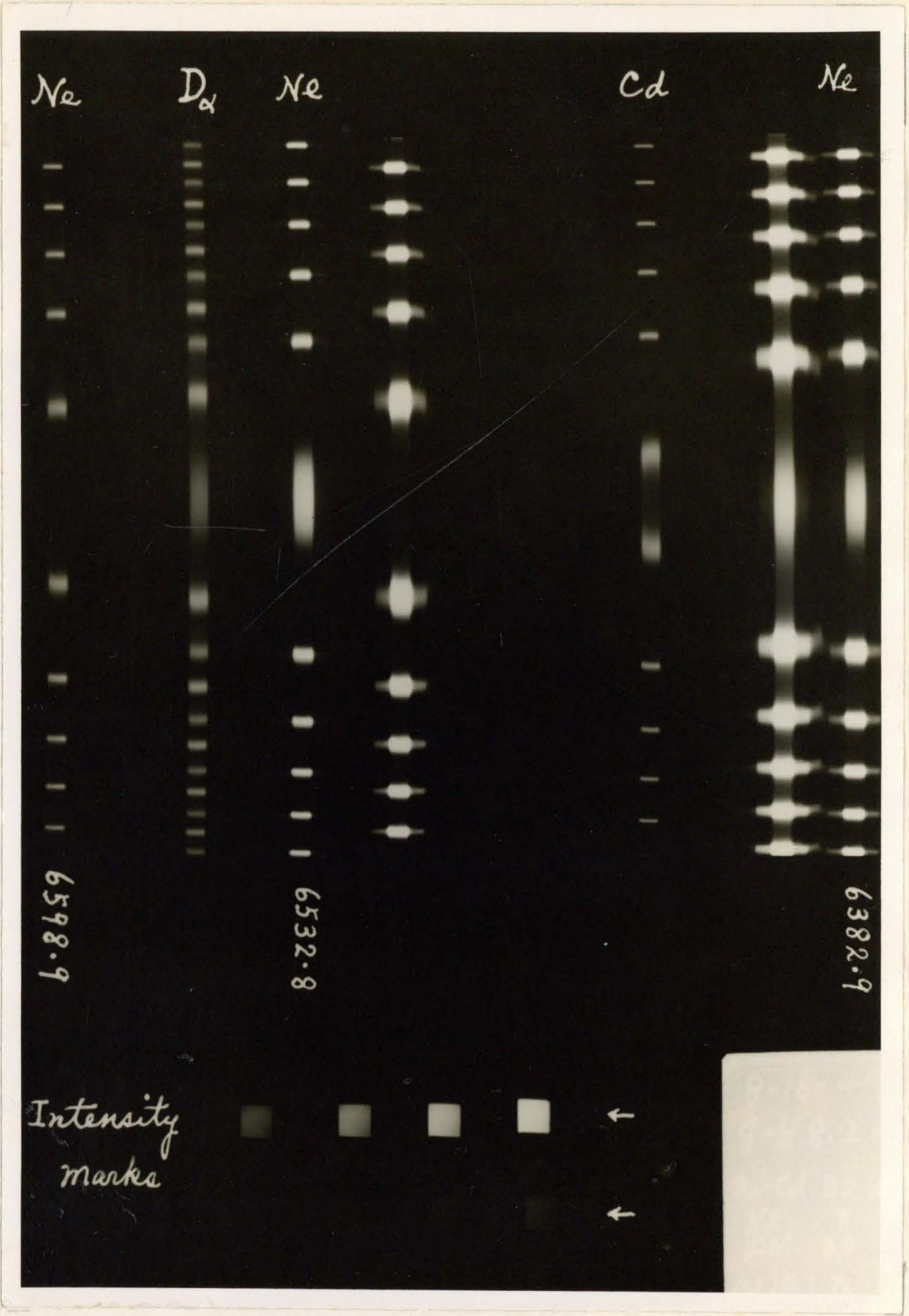

Fig. 4. Photograph of a spectroscopic plate with the interferometer patterns of Cd, H-alpha and Ne lines and the intensity marks. White color on the photograph corresponds to black color on the plate.

3. THE LIGHT SOURCE FOR H-ALPHA AND D-ALPHA LINES

3.1 The Discharge Tube and Its Cooling Method

In the first stage of this work, an electrodeless hydrogen discharge tube[10] excited by a high-frequency oscillator was tried. It was found to have several disadvantages. One of these was observed in trying to photograph simultaneously the H-alpha line and the cadmium standard line, in which a half-silvered mirror was used. This naturally cut down the effective intensity of the spectral lines. In this case, the hydrogen discharge tube was not able to provide an H-alpha line of sufficient intensity to give a satisfactory interferometer spectrogram. Futhermore, the discharge in the tube produced a dircular image on the spectrographic slit, which caused the latter to be unevenly illuminated. A third disadvantage arose from the large bore of the tube. Its diameter of one inch was too large for an efficient cooling of the hydrogen gas inside, and the H-alpha line thus obtained was not as sharp as desired. Therefore, another hydrogen discharge tube had to be designed.

Fig. 5 shows the new hydrogen discharge tube inside a Dewar flask. It resembled a Geissler tube in that its central part consisted of a capillary, 6 cm. long. To insure a rapid cooling of the tube in liquid air, a thin-walled capillary with a bore and

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[10] C. W. Hsueh, Rev. Sci. Inst. 14, 251 (1943).

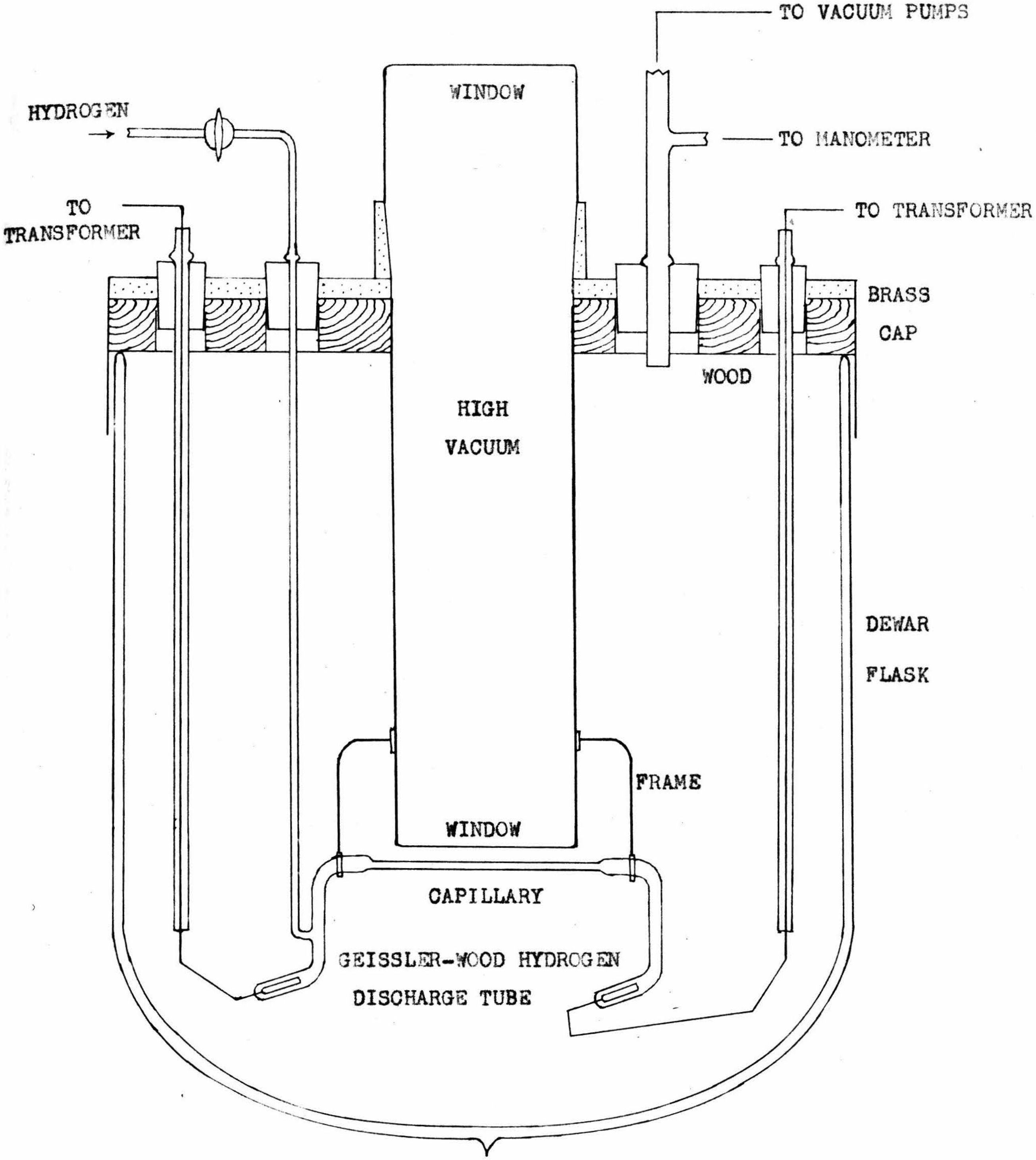

Fig. 5. The Geissler-Wood hydrogen discharge tube cooled in liquid air under low pressure.

outer diameter of 3 mm. and 5 mm. respectively was chosen. By thus concentrating the discharge in a narrow space, the capillary had the advantage of increasing the intensity of H-alpha. The new tube also had some of the features of a Wood's tube in being longer than the Geissler tube and having a smaller diameter. It seems proper to call it the Geissler-Wood hydrogen discharge tube. A transformer was used to run it. The voltage drop across the tube was about 1,200 volts and the power consumed by the tube was approximately 20 watts. The tube was protected by means of two 9000-ohm resistors connected in series.

Inasmuch as the light emitted from the capillary discharge was used for taking spectrograms, the construction of the capillary needed special considerations. In general, when a discharge tube is run by a transformer or a generator, the hottest part of the tube is around the electrodes. Hence, to keep down the heating effect of the discharge on the central capillary of the tube, it is better to have the electrodes far away from the capillary. This was one of the features from the Wood's tube, which was adopted in our modification. To decrease the Stark-effect at the capillary, the two ends of the tube were bent towards the same side of the capillary, which, thereby, reduced the electric field around that part.

In order to reduce the Doppler-effect width of the H-alpha and D-alpha lines and to make their fine structure observable, the discharge tube was cooled with rapidly evaporating liquid air which, due to its low temperature, cut down the temperature motion of the atoms. A diagram of the experimental arrangement is shown in Fig. 5. Liquid air was contained in a Dewar flask of 4.5-liter capacity. The opening of the flask was closed with a brass cap and sealed air-tight with layers of rubber tape, 3/4 inch wide, painted with G. E. Glyptal No. 1202. A layer of wood, 2 cm. thick, was placed under the cap to improve heat insulation. On top of the cap are connections to vacuum pumps and to the manometer, leads to the transformer, inlet for hydrogen or deuterium gas, and holes for pouring in liquid air. Experience proved that rapidly evaporating liquid-air not only provided much lower temperatures than liquid air at atmospheric pressure, but also lasted longer. This apparent paradox can be explained in the following way. The speed of evaporation of the liquid air in a Dewar flask depends upon the rate at which the surrounding heat is conducted into the liquid air. When liquid air is under low pressure, and thus protected by a better insulation, the heat entered is less than that under atmospheric pressure.

The light of the capillary discharge situated at the bottom of the liquid-air flask, was transmitted through a high-vacuum window, which was an evacuated and sealed glass pipe, 27 cm. long and 5 cm. in diameter. This highly evacuated window had the desirable quality of being both a good transmitter of light and an excellent heat insulator at the same time. The lateral side of the glass pipe was covered with a layer of black tape to cut off stray light. The capillary of the discharge tube was placed under the vacuum glass pipe, perpendicular to the long axis of the latter. Thus, the line of observation was normal to the direction of the discharge current. In this way, the Doppler effect was further reduced, since the observation was made perpendicular to the motion of the light-emitting atoms. When the interferometer pattern of the D-alpha line, shown in Fig. 4 and obtained with the above arrangement, is compared with that in the paper of Shane and Spedding[11], the former appears to be much sharper.

Several precautions in the use of the tube may be mentioned. For example, no liquid, like acids, alcohol or water, should be used to clean the Geissler-Wood discharge tube, because liquids contaminate the tube and decrease the efficiency of producing the H-alpha line. After the tube has been used for a long time, a decrease in the intensity of the H-alpha line is also observed. This is due to accumulation of impurities condensed within the tube. Sometimes, the efficiency can be recovered by evacuating the tube at room temperature. If this method fails, then it is

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11. C. D. Shane and F. H. Spedding, Phys. Rev. <u>47</u>, 34 (1935).

better to make a new tube, since a good glass-blower can make a new one within a few hours. Because mercury vapor interferes strongly with the production of a strong H-alpha line, care should be taken to prevent mercury vapor from entering the tube by means of an efficient liquid-air trap. The current used in exciting the tube should be chosen in accordance with the time of exposure and the amount of hypersensitizing of the spectrographic plate. For example, when the plate is baked for 26 hours at 50°C and the exposure time is 30 minutes, the discharge current for a newly made tube should be around 14 milliamperes.

Many workers on the D-alpha line used only the vapor of heavy water (D_2O) in their discharge tube to produce D-alpha discharge. However, according to the writer's experience, pure deuterium gas gave much stronger D-alpha than the water vapor, especially when cooled in liquid air. This was also true with hydrogen. Besides, the intensity ratio of the two main component-groups would have nearly the theoretical value, when gas, rather than water vapor, was admitted to the tube. The work of Spedding, Shane and Grace[12] supported this fact. Therefore, pure deuterium and hydrogen gases were used throughout this work.

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[12] Spedding, Shane and Grace, Phys. Rev. 47, 38 (1935).

3.2 Preparation of the Deuterium Gas

The hydrogen gas used in the discharge tube was obtained from the electrolysis of water to which ten per cent of concentrated sulfuric acid was added. The gas was purified by passing through a liquid-air trap. However, it did not seem feasible to prepare deuterium gas by the electrolysis of heavy water, because too much heavy water was needed to fill the available electrolysis apparatus, especially in view of the scarcity of heavy water during the War. Hence, another method of preparing the deuterium gas had to be developed.

Fig. 6 shows the apparatus for generating deuterium gas from the reaction of deuterium oxide with sodium. The sodium metal used was supplied by the Mefford Chemical Company, Los Angeles, and was contained in an air-tight tin-can, free from oil. It was placed in the glass basket, 5 cm. above the heavy water. When the vapor of the deuterium oxide comes in contact with the sodium metal, a chemical reaction takes place liberating deuterium gas and depositing sodium deuteroxide ($NaOD$) on the surface. The sodium deuteroxide, similar to sodium hydroxide, has the property of absorbing water vapor. So the reaction continues until all the sodium, which can be reached by the water vapor, changes into deuteroxide. The chief advantage of this method over the electrolysis procedure mentioned above lies in its

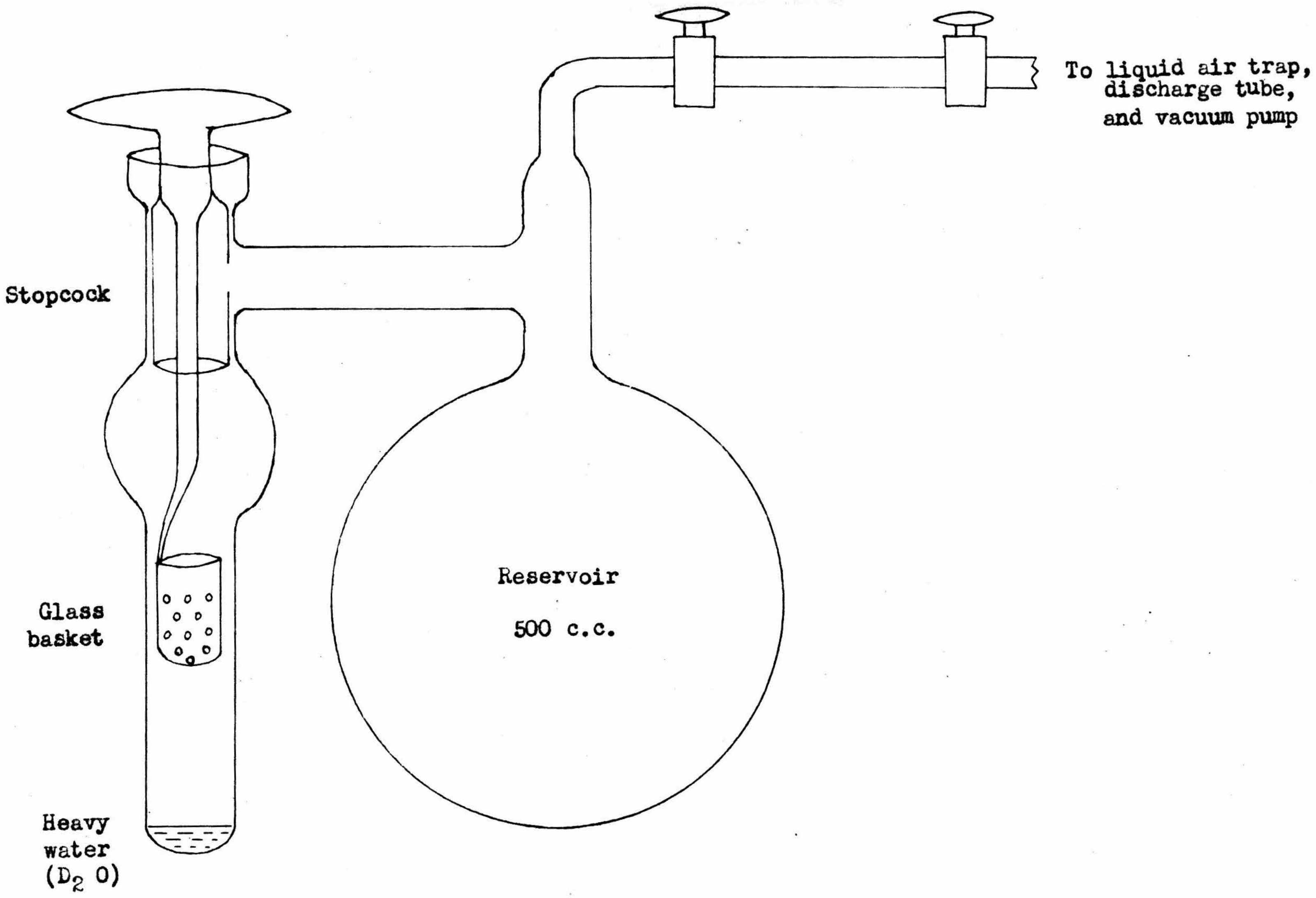

Fig. 6. Generator for the deuterium gas

economical use of heavy water. Only one gram of heavy water was required each time, thereby generating deuterium gas sufficient for ten days' work or longer.

The procedure is as follows. First, the apparatus was cleaned by evacuation until it was free from water or organic vapor. One gram or less of heavy water was poured into the apparatus, and two grams of clean sodium, cut into small pieces, was placed in the glass basket. After replacement of the stopper, the reaction flask was partially immersed in liquid air, which froze the water and stopped the reaction. The apparatus was then evacuated. Removal of the liquid-air bath gave rise to the generation of deuterium gas. When the apparatus got warm, deuterium gas was liberated. After sufficient gas was obtained, the apparatus was cooled again in liquid air. In this way, the heavy water could be preserved for future use.

4. OPTICAL SET-UP AND THE PROCEDURE FOR TAKING SPECTROGRAMS

A plane reflecting grating of 48,000 lines per inch was used for the dispersing system, while a Fabry-Perot interferometer, as a resolving instrument. The interferometer consisted of two circular optical flats, 11.5 cm. in diameter, and was heavily silvered. For studying the H-alpha and D-alpha lines, four different interferometer gaps, 7.6, 7.8, 8.0 and 8.2 cm. respectively, were used. For finding the phase change correction at reflection, an interferometer gap of 21 mm. was used. Because the neon lines are much sharper than the H-alpha line, two neon lines, 6532.8824 A and 6598.9529 A, one on each side of the H-alpha or D-alpha line, were used in the determination of the phase-change correction.

To avoid errors introduced by changes in environmental factors, the light sources for H-alpha or D-alpha, for cadmium standard line, and for neon lines were projected simultaneously on the interferometer and the grating. The detailed arrangement is shown in Fig. 7. The room where the spectrograms were photographed, was located in the basement of the Norman Bridge Building with no windows to the outside. Because of this favorable location, the temperature around the interferometer remained constant to within 1/20 of a degree Centigrade during the period of 30 minutes' exposure. To decrease the effects of vibrations caused by the transformers and the vacuum pumps, the

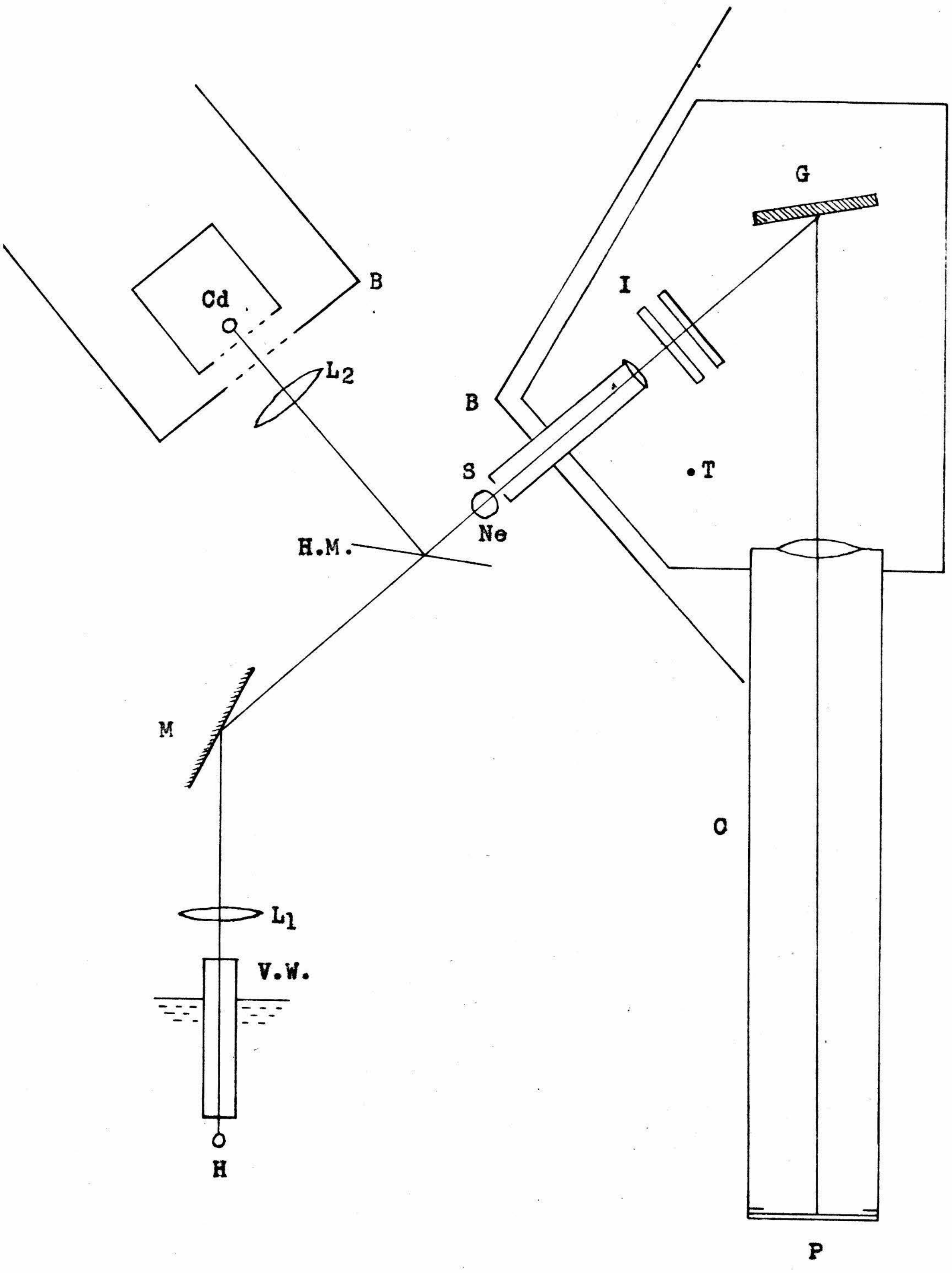

Fig. 7. Optical set-up for taking spectrograms

Fig. 7. Optical set-up for taking spectrograms

B - Wall of wooden board.

C - Camera of the spectrograph with lens of 200 cm. focal length.

Cd - Light source for the standard cadmium line.

G - Plane reflecting grating, 48,000 lines per inch.

H - Hydrogen discharge tube.

H.M. - Half-silvered mirror.

I - Fabry-Perot interferometer.

L_1, L_2 - Lenses for focusing the light sources on the spectrograph slit.

M - Mirror.

Ne - Neon discharge tube.

P - Spectrograph plate.

S - Slit of the spectrograph.

T - Thermometer.

V.W. - Vacuum window.

spectrograph, the transformers and the light sources were cushioned with felt and the vacuum pumps, with an additional layer of paper, 1.5 inch thick. The effect of the heat from the furnace of the Michelson lamp on the interferometer is eliminated by placing the interferometer in a box and by erecting a wall of wooden board around the furnace and the grating-interferometer, respectively.

Throughout this work, Eastman spectroscopic plates type 103 H-alpha and size 5 by 7 inches, were used. To increase the speed of the plates, each plate was hypersensitized by heat treatment[12], a few hours before use. In the heat treatment, the plate was wrapped in layers of black paper and tin foil, and packed in a cardboard box, which was placed in an electric oven, kept at a temperature of 50°C., for a period of around 26 hours. The exposure time for H-alpha or D-alpha, together with cadmium line, was 30 minutes, and for neon lines, was from 4 to 8 minutes. During this 30 minute period, readings of the atmospheric pressure, the temperature around the interferometer, and the humidity, were taken, which were needed for the calculation of the wavelength correction to normal air conditions. Immediately after that, the plate was exposed to the intensity-mark maker described in Section 5, for also 30 minutes. Then, it was developed in a high

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12. I. S. Bowen and L. T. Clark, Jour. O. S. A. <u>30</u>, 508 (1940).

contrast developer, D-19, for 3.5 minutes, with constant agitation. To preserve the red-sensitive plates from fogging, they were stored in a refrigerating room, when not in use. Fig. 4 (Page 15) shows a photograph of a sample plate.

5. CALIBRATION OF SPECTROSCOPIC PLATES AND THE INTENSITY RATIO

The relation between the blackness of the photographic plate and the intensity of the incident light is expressed by the characteristic curve of the plate, also called the H and D curve. The characteristic curve is determined by the calibrations with intensities of known ratio. One of the methods to produce the various intensities is the stepweakener. The stepweakener used in this work consists of twelve holes on a brass block, 1 $\frac{3}{4}$ inches wide, 2 inches long and 1 $\frac{1}{2}$ inches high. The diameter of the holes varies from 0.537 mm. to 6.312 mm. The incident intensities are proportional to the area of the holes, or the square of their diameters. Each hole is covered by a small lens having a focal length equal to the height of the block, and on top of the twelve small lenses is a larger lens which covers all of the twelve holes. Above the block is an illuminated square, at a distance, from the large lens, equal to its focal length. Under the block is the spectroscopic plate to be calibrated. An image of the illuminated square is formed on the plate under each hole. After sufficient exposure and development, twelve black squares appear on the plate. A sample of the intensity marks is shown in Fig. 4 (Page 15). The H and D curve is obtained by plotting the density of the black mark against the square of the diameter of the corresponding hole, on a log-long graph.

The characteristic curve of a photographic plate depends upon the time of exposure, the developing of the plate and the wavelength of the incident light. In order to find the intensity of the various H-alpha components accurately, the time of exposure of the H-alpha line and of the intensity marks was the same. The developing was also the same, because they were on the same spectroscopic plate. The light used to illuminate the square came from a G. E. 25-watt Mazda ruby lamp passing through a Wratten No. 29 filter. The spectrum showed that the light from such an arrangement consisted of a narrow band with the central maximum at the H-alpha line, 6563 A. Hence, it was suitable to be used to calibrate the plate for the spectral region around the H-alpha line. Opal and ground glass were used to cut down the intensity of the ruby lamp. This was required in order to match the intensity of the band emitted by the Mazda lamp with that of H-alpha. Fig. 8 shows the detailed arrangement for making the intensity marks.

The procedure for finding the intensity ratio of the two main components of the H-alpha or D-alpha line is as follows. After the microphotometer curves of an H-alpha line was made, the densities of the intensity marks on the same plate were read directly on the microphotometer. There were in general eight or ten orders of the H-alpha line on each microphotometer curve.

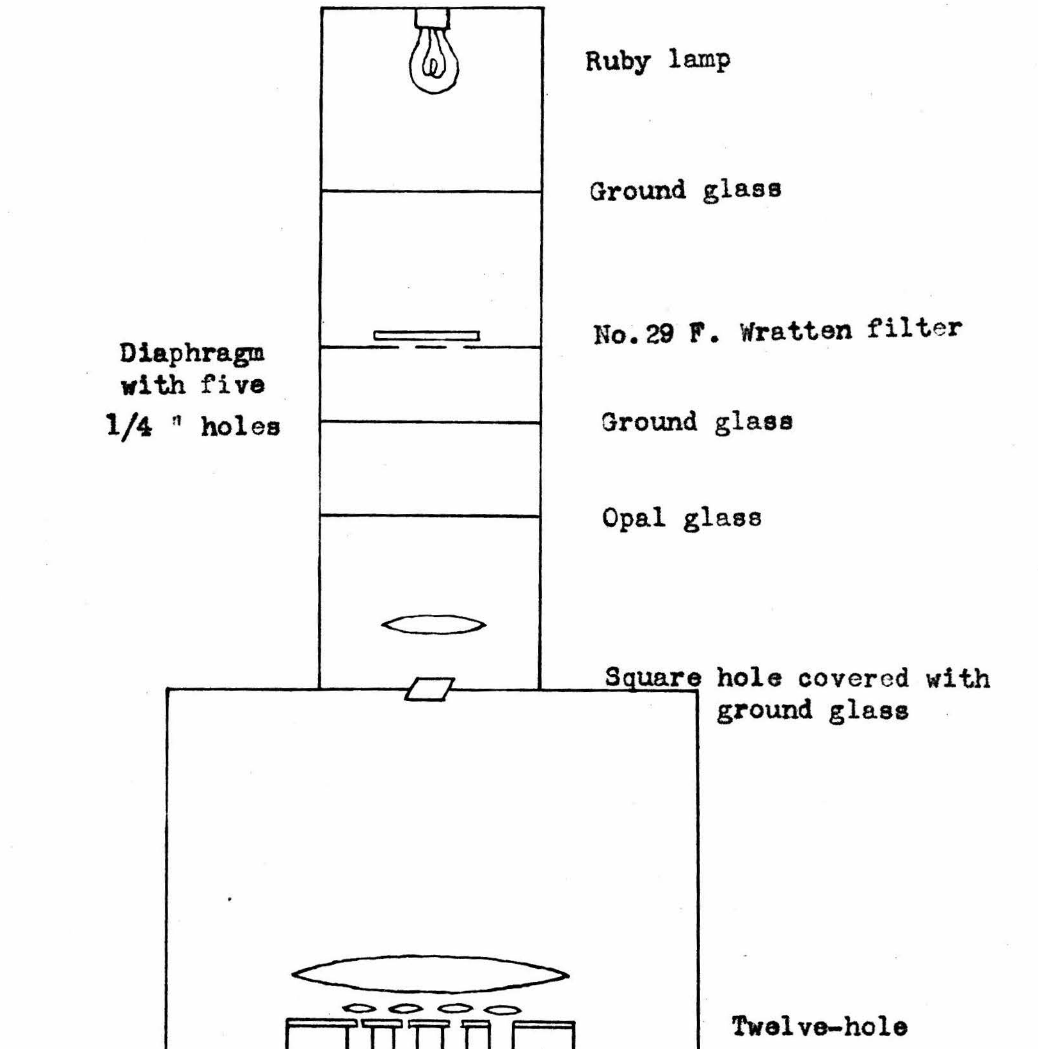

Fig. 8. Arrangement for photographing intensity marks to calibrate the spectroscopic plate

Each order showed two main components of the H-alpha line, of which the stronger is called the (145) component-group and the weaker, the (23) component-group. For each order, the heights of the two maxima above the line of the common background, which represent the densities of the two groups of components, were measured. The average value of the eight orders gave the density of the (145) and the (23) component-group, respectively. The corresponding intensity was found from the characteristic curve of the spectroscopic plate, and from these intensity values, the intensity ratio was calculated. The results of the intensity ratio for the H-alpha and D-alpha lines appear in Section 7.1 .

6. MEASUREMENT OF WAVELENGTH

6.1 General Principle

Let d be the separation of the two interferometer plates, and λ be the wavelength of a spectral line. The equation for the Fabry-Perot interferometer[13] gives, at the center of the circular fringes,

$$P \lambda = 2 d \qquad \text{.........} (1)$$

where P is the order of interference at the center of the ring system, but not necessarily a whole number. Hence, if the standard line is defined by $\lambda_o = 6438.4696$ I.A., the wavelength of another line can be found from the relation,

$$P \lambda = P_o \lambda_o = \text{constant} \qquad \text{.......} (2)$$

The problem of measuring the wavelength λ becomes that of finding the values of P and P_o . Let us write

$$P = n + \epsilon \qquad \text{.........} (3)$$

where n is the integral part of the number P, and ϵ represents the fractional part. Equation (2) can then be written as

$$\lambda = \lambda_o (n_o + \epsilon_o) / (n + \epsilon) \qquad \text{.........}(4)$$

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[13] G. S. Monk, Light (McGraw-Hill Company, New York, 1937), first edition, P. 155 ; K. W. Meissner, Jour. O. S. A. 31, 409 (1941).

The value of the fractional order of interference, ϵ, of a line λ is obtained by measuring the diameters of the interferometer pattern of that line, sample of which are shown in Fig. 4. The value of the integral part of the order of interference, n, is found from the approximate values of the separation, d, and of the wavelength, λ. The separation, d, of the Fabry-Perot interferometer can be measured with a micrometer ; while the approximate value of λ can be obtained from grating measurement, or other methods. Detailed procedures will be described in the following sections.

6.2 Computation of the Fractional Order, ϵ

6.2.1 Equation $D_k^2 = a\,k + a\,\epsilon$ and Its Derivation

In the above equation, D_k represents the diameter of the kth circular fringe, and a is a constant for all of the fringes of a given spectral line.

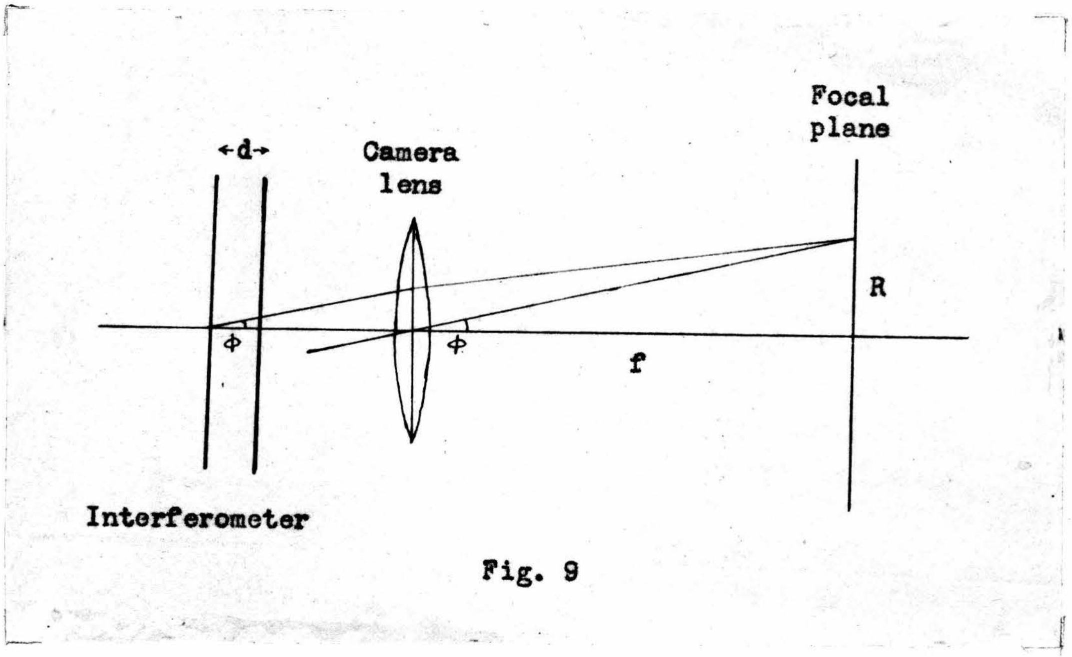

Fig. 9

According to the equation for the Fabry-Perot interferometer, the order of interference for a circular bright ring of radius R and for the spectral line of wavelength λ is given by the formula,

$$q = 2\,d\,\cos\phi\,/\,\lambda \qquad \text{.........} \; (5)$$

where q has only integral values. If f denotes the focal length of the camera lens of the spectrograph (Fig. 9), the cosine of the angle of incidence, ϕ, for rays forming the fringe of radius R, is given by the equation,

$$\cos\phi = \frac{f}{\sqrt{f^2 + R^2}}$$

$$= \left(1 + \frac{R^2}{f^2}\right)^{-\frac{1}{2}}$$

$$= 1 - \frac{R^2}{2f^2}$$

$$= 1 - \frac{D^2}{8f^2} \qquad \ldots\ldots\ldots (6)$$

In equation (6), R^2/f^2 is of the order 0.0001. As a consequence, all terms of the fourth power or higher can be neglected. Equation (1) can also be written as

$$P = 2d/\lambda \qquad \ldots\ldots\ldots (7)$$

Substituting (6) and (7), equation (5) gives

$$q = \frac{2d}{\lambda} - \frac{d}{4\lambda f^2} D^2$$

$$= P - \frac{D^2}{a} \qquad \ldots\ldots\ldots (8)$$

where a represents the quantity, $4\lambda f/d$, and remains constant for all of the fringes of the spectral line λ.

Let us find out the relation between the integer, n, in equation (3) and the order of interference, q, in equation (5).

As $\cos\phi$ is a decreasing function of ϕ and of the diameter D by inspection of Fig. 9, the number q given in equation (5) is also a decreasing function of D. So the order of interference, q_o, for the bright fringe of the smallest diameter, has the largest value and equals to n. Thus, we have

$$q_o = n ,$$

and for the first fringe, $q_1 = q_o - 1 = n - 1$,

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

and for the kth fringe, $q_k = q_o - k = n - k$ ...... (9)

By combining (8) and (9), we have

$$n - k = P - D_k^2 / a ,$$

which may be written as

$$D_k^2 / a = k + (P - n)$$

substituting P from (3), $= k + \epsilon$

Multiplying both sides by a, we get the desired equation,

$$D_k^2 = a k + a\epsilon \qquad \text{......} (10)$$

6.2.2 The Best Value for ϵ

For each circular fringe, there is a value for ϵ , given by equation (10). Naturally, the question arises, which value of ϵ should be used in equation (4) to calculate the wavelength. The best value for ϵ is usually found by the Method of Least squares. In equation (10), let

$$e = a\epsilon \qquad \text{.........} \ (11)$$

and it becomes $D_k^2 = a\,k + e$

In the language of the Method of Least Squares, the residual of the square of the diameter of a fringe is given by

$$D_k^2 - a\,k - e$$

Let M represent the sum of the squares of the residuals and N, the number of fringes of a spectral line, the diameters of which have been measured. Then

$$M = \sum_{K=1}^{N} \left(D_K^2 - aK - e \right)^2 \qquad \text{..} \ (12)$$

according to the Principle of Least Squares, the most probable system of values of the unknown is that which renders the sum of the squares of the residuals a minimum. In order that the function M has a minimum value, we must have

$$\frac{\partial M}{\partial a} = 0$$

and $$\frac{\partial M}{\partial e} = 0 \qquad \ldots\ldots (13)$$

Solving the above two equations for a and e, we get

$$a = \frac{2S_2 - (N+1)S_1}{N(N-1)(N+1)} \qquad \ldots\ldots (14)$$

$$e = \frac{3S_2 - (2N+1)S_1}{N(1-N)} \qquad \ldots\ldots (15)$$

The symbols, S_1 and S_2, are used to represent the expressions

$$S_1 = \sum_{K=1}^{N} D_K^2 \quad ; \quad S_2 = \sum_{K=1}^{N} K D_K^2 \qquad \ldots. (16)$$

After the values of a and e are found from equations (14) and (15), the best value for ϵ is computed from the equation

$$\epsilon = e / a \qquad \ldots\ldots. (17)$$

The formulae used most often to calculate a and e are those for N = 3, 4, and 8, respectively. They are listed as follows :

$$N = 3 \left\{ \begin{aligned} a &= \frac{1}{2}(S_2 - 2S_1) \\ e &= \frac{1}{3}(7S_1 - 3S_2) \end{aligned} \right.$$

$$N = 4 \left\{ \begin{aligned} a &= \frac{1}{10}(2S_2 - 5S_1) \\ e &= \frac{1}{2}(3S_1 - S_2) \end{aligned} \right.$$

$$N = 8 \left\{ \begin{aligned} a &= \frac{1}{84}(2S_2 - 9S_1) \\ e &= \frac{1}{28}(17S_1 - 3S_2) \end{aligned} \right.$$

6.2.3 Considerations in Measuring the Diameter of the Fringes

The accuracy of the value of ϵ, and thus that of the wavelength, depends upon the reliability of the values for the fringe diameters. Consequently, the latter should be measured as accurately as possible. Inasmuch as a spectral line has a definite width, the fringe marks which appear on its interferometer pattern are not mathematical lines, but narrow bands. The narrower the spectral line, the sharper are the corresponding fringe marks. This is the most important reason why, in designing the light sources, methods were used to obtain as sharp a spectral line as possible.

In order to locate easily and accurately the reference points for measuring the fringe diameters, microphotometer curves were made for the spectral lines. The microphotometer used was the Koch-Goos microphotometer, made by A Kruss Co., Hamburg. It takes a 9 cm. x 24 cm. photographic plate. As the interferometer pattern of the spectral line was 8.4 cm. long, a horizontal magnification of 2 was used. This magnification further increased the accuracy of measuring the fringe diameters. On each of the H-alpha plates for the determination of the wavelength of H-alpha, microphotometer curves were made for the lines, H-alpha, Cd standard line, and two neon lines, 6532.8824 A and 6598.9529 A. A sample of the microphotometer curve for the

H-alpha line is shown in Fig. 10. In the case of the D-alpha plates for the determination of the wavelength of D-alpha, microphotometer curves were made for the lines, D-alpha, Cd line, and the same two neon lines. A sample of the microphotometer curve for the D-alpha line is shown in Fig. 11. The two neon lines were used to determine the reflection phase-change correction for the H-alpha and D-alpha lines, and to check the values of the n's to be described in Section 6.3 .

Different fringes of a single line are not of the same width, which varies inversely with the diameter of the fringe. If a spectral line had more fringes than needed, the sharper ones were used for the measurements, because they gave a greater accuracy in locating the reference points. In selecting the reference points, Birge's statement[14] was taken into account, i.e., if the upper part of the curve is used to locate its center line, component 5 of H-alpha has a negligible influence and the center line lies exactly 0.0036 cm^{-1} toward the red of component 1. Since the correction 0.0036 cm^{-1} was to be used in the calculation of the Rydberg constants, his opinion was followed. Therefore, the maximum points of the microphotometer curves, or the middle points of the horizontal levels which

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[14] R. T. Birge, Phys. Rev. 60, 772 (1941).

intersect the upper part of the curve, were taken as the reference points for the measurements. The horizontal levels can be seen in the microphotometer curves shown in Fig. 10 and Fig. 11.

A comparator readable to 0.0005 mm. was used to measure the diameters. For each reference point, readings were taken in two careful settings. One setting was made when the comparator-microscope was travelling in one direction and the other setting, when the microscope was travelling in the opposite direction. The diameter of a fringe was the difference between the readings for the two reference points of that fringe.

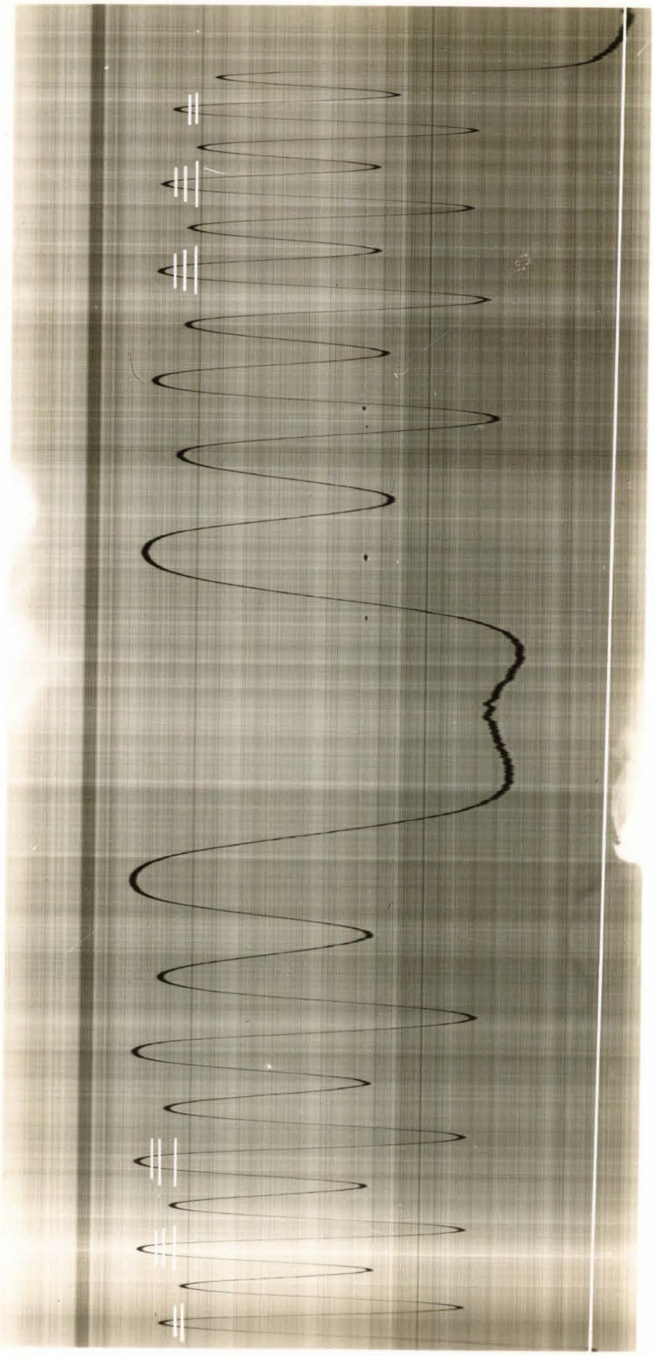

Fig. 10. Microphotometer curve for the H-alpha line

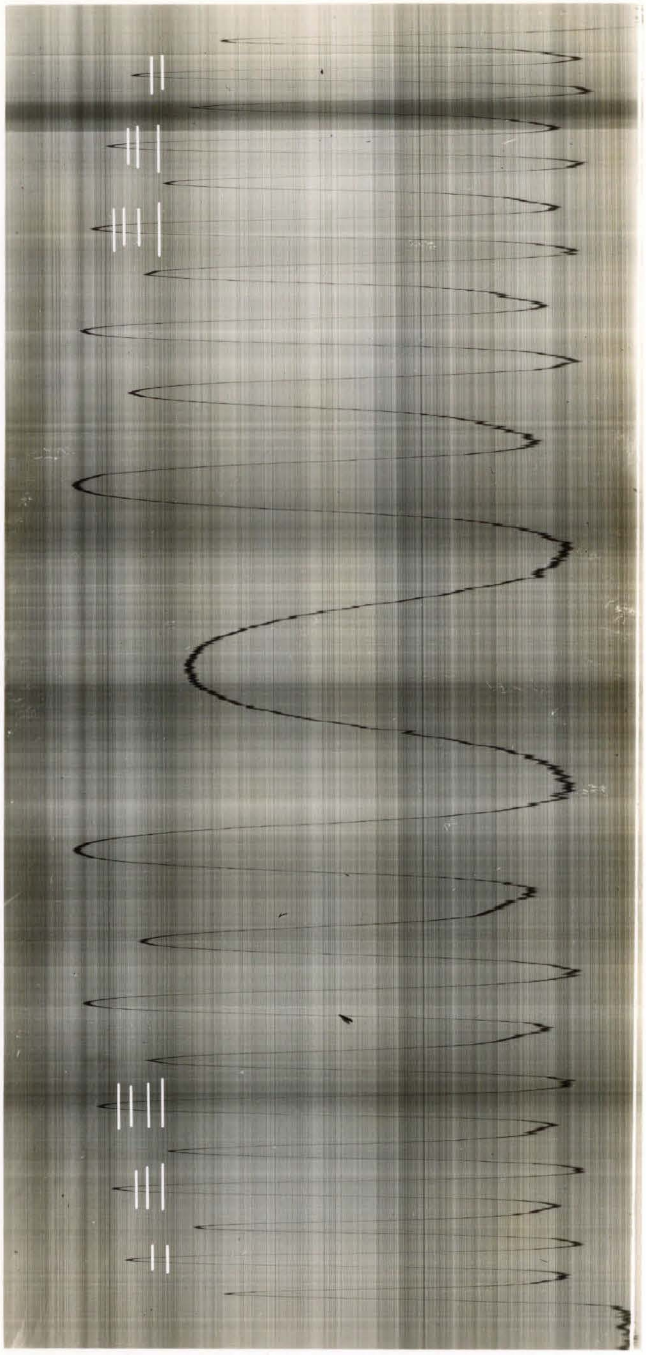

Fig. 11. Microphotometer curve for the D-alpha line

6.3 Procedure for Finding n

From equations (1) and (4), we have

$$\lambda\ (n + \epsilon) = \lambda_o\ (n_o + \epsilon_o) = 2\ d \qquad \ldots\ldots (18)$$

where the values for ϵ and ϵ_o are computed from equations (14), (15) and (17). An approximate value of the separation d of the interferometer can be found by measuring with a micrometer the length of the three pillars of the separator. A tentative value for n_o can be obtained by dividing the d by $\lambda = 6438.4696$. Then using the known value of the wavelength λ, we can calculate the ratio λ_o / λ. For the H-alpha line, Houston's values were used. For D-alpha line, the value of the wavelength calculated from the wave number of Drinkwater, Richardson and Williams was used. For neon lines, the values given in Harrison's Wave-Length Tables were used.

By multiplying the ratio λ_o / λ by the number $(n_o + \epsilon_o)$, the numbers n and ϵ are obtained. Next, we change the value of n_o by 1, 2, 3, ... 10, 20, ... etc., until the value of ϵ agrees with that calculated from the fringe diameters. The same process is repeated for all the lines on a spectroscopic plate, until all the ϵ's agree with the calculated numbers. Then this set of n's should be used for computing the λ's by means of equation (4).

6.4 Correction to Normal Air Conditions

The unit of wavelength which is called the International Angstrom is defined as

I.A. = the wavelength of the red Cd line in dry air at 15°C., and 760 mm., with $g = 980.67$, divided by 6438.4696 .

This unit is used as a basis for the precise measurement of all other wavelengths. Variations in the conditions of air appreciably affect the absolute values of the wavelengths measured in air, especially when the spectral line is far away from the red cadmium line. Hence, when wavelength measurements are made under air conditions different from those specified in the above definition (normal air conditions), it is necessary to apply corrections, the calculation of which will be described below.

Let λ be the wavelength of a spectral line to be measured and μ be the refractive index of air for this wavelength, under experimental conditions. λ_o and μ_o then are the analogous quantities for the standard line under the same conditions. The orders of interference, P and P_o , measured under the actual conditions, are connected by the relation :

$$P \lambda = P_o \lambda_o = 2d, \quad \text{or} \quad P_o / P = \lambda / \lambda_o \quad \ldots.. (19)$$

However, in calculating λ, the value of the standard wavelength was taken as λ_{on} , the value under normal air conditions, and the formula, $\lambda = \lambda_{on} P_o / P$, was used. Since the correction is the difference between the exact value λ_n under normal air conditions, and the calculated one for λ, it is given by

$$\Delta = \lambda_n - \frac{P_o \lambda_{on}}{P}$$

which, by using the relation (19), may be written as

$$\begin{aligned}\Delta &= \lambda_n \left(1 - \frac{P_o \lambda_{on}}{P \lambda_n}\right) \\ &= \lambda_n \left(1 - \frac{\lambda \lambda_{on}}{\lambda_o \lambda_n}\right) \qquad \text{..... (20)}\end{aligned}$$

Now, the refractive index of air, μ, and the wavelength, λ, are related each other as follows :

$$\mu \lambda = \mu_o \lambda_o = \text{constant},$$

from which we have

under experimental conditions, $\dfrac{\lambda}{\lambda_o} = \dfrac{\mu_o}{\mu}$

and under normal conditions, $\dfrac{\lambda_{on}}{\lambda_n} = \dfrac{\mu_n}{\mu_{on}}$ ... (21)

Substituting (21) into (20),

$$\begin{aligned}\Delta &= \lambda_n \left(1 - \frac{\mu_o \mu_n}{\mu \mu_{on}}\right) \\ &= \lambda_n \frac{\mu \mu_{on} - \mu_o \mu_n}{\mu \mu_{on}} \qquad \text{..... (22)}\end{aligned}$$

Let $r = \mu - 1$ be the refractivity of air. Replacing μ by r in equation (22) and neglecting terms of the second order and higher, we get

$$\Delta = \lambda_n \left[(r_{on} - r_n) - (r_o - r) \right] \qquad \ldots\ldots (23)$$

As the difference between λ_n and λ is so small, we can substitute λ for λ_n in equation (23) for all the calculations. Thus we have

$$\Delta = \lambda \left[(r_{on} - r_n) - (r_o - r) \right] \qquad \ldots\ldots (24)$$

In the above equation, r_{on} and r_n represent the refractivity of air for the standard wavelength λ_o and the wavelength λ respectively under normal air condtions (dry air, at 15°C and 760 mm) ; r_o and r represent the refractivity of air for λ_o and λ respectively under experimental conditions. The value of the r's are found from Barrell and Sear's equation of 1939[15]. This equation for the refractivity of the moist atmospheric air is of the form :

$$\begin{aligned} r_{t,p,f} \times 10^{6} &= (\mu_{t,p,f} - 1) \times 10^{6} \\ &= \left[0.378{,}125 + \frac{0.002{,}141{,}4}{\lambda^2} + \frac{0.000{,}017{,}93}{\lambda^4} \right] \\ &\quad \times \frac{p\{1 + (1.049 - 0.0157t)p \times 10^{-6}\}}{1 + 0.003661t} \\ &\quad - \left[0.0624 - \frac{0.000{,}680}{\lambda^2} \right] \frac{f}{1 + 0.003661t} \end{aligned}$$

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15. H. Barrell and J. E. Sears, Phil. Trans. Roy. Soc. No. 786, <u>238</u>, 52 (1939).

where $t^\circ C.$ represents the temperature of air between 10° and $30^\circ C.$

p mm. Hg. ..... the barometric pressure between 720 and 800 mm.

f mm. Hg. ..... absolute humidity of air, less than 20 mm.

and λ ..... the wavelength in vacuum, expressed in microns.

After the correction Δ is found by means of equation (24), the desired value of the wavelength λ_n under normal air conditions is obtained by adding Δ to the value of λ, given by interferometer measurement. The following table illustrates the magnitude of the corrections.

Table 1

Correction to normal air conditions

Plate No.	Line	$t^\circ C.$	p mm. Hg.	f mm. Hg.	Correction I.A.
64	H-alpha	23.8	750	8.3	0.0000267
73	H-alpha	24.7	744	11.2	0.0000365
76	H-alpha	22.7	746	10.1	0.0000377
27	D-alpha	23.4	743	15.0	0.0000309
34	D-alpha	23.3	745	14.5	0.0000290
48	D-alpha	25.5	746	16.5	0.0000259

The determination of the correction for the phase change at reflection has been mentioned in Section 4.

7. RESULTS

7.1 Intensity Ratio

All of the exposures for H-alpha and for D-alpha were taken when the discharge in the hydrogen tube was at its maximum intensity. That condition was ascertained by the purple red color of the capillary discharge, by the strong intensity of the red H-alpha line as viewed with a direct-vision spectroscope, and by the maximum discharge current as measured with a milliammeter. Ordinary hydrogen discharge is bluish in color but, when the discharge is strong, it becomes purple red. The pressure of the hydrogen gas in the discharge tube was found to be around 0.4 mm. Hg. during the period of maximum discharge.

According to Dirac's theory of the hydrogen atom, or the Sommerfeld's fine structure formula, the H-alpha line, or the D-alpha, consists of five components. Following William's assignment[16], these have been named the 1, 2, 3, 4, and 5 components in decreasing order of their intensities. However, on account of the overlapping due to the Doppler-effect width of the components, only two groups of components can be resolved. The group with the stronger intensity is composed of the 1, 4, and 5 components, while the weaker group is composed of the 2 and 3 components. Theoretically, the value of the intensity

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[16] R. C. Williams, Phys. Rev. 54, 559 (1938).

ratio is given by [17] I(23) / I(145) = 0.806 .

The method described in Section 5 was used to find the experimental values of the intensity ratio. The results are tabulated in tables 2 and 3, in which the precision measure was computed according to the method described by Margenau and Murphy[18]. It is equal to the average deviation from the mean divided by the square root of the number of measurements.

The results of the measurements on the intensity ratio for H-alpha and D-alpha suggest the following conclusion : The value of the intensity ratio will be equal to the theoretical value, if pure hydrogen, or deuterium, gas is used in the discharge tube and the discharge is at its maximum illumination.

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17. W. V. Houston and Y. M. Hsieh, Phys. Rev. 45, 271 (1933).
18. H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry, (D. Van Nostrand Company, New York, 1943), p. 497.

Table 2

Intensity ratio for the H-alpha line

Plate No.	Interferometer separation, mm.	Intensity ratio I(23) / I(145)
75	7.6	0.816
76	7.6	0.820
72	7.8	0.824
73	7.8	0.810
77	7.8	0.822
80	8.0	0.789
81	8.0	0.800
62	8.2	0.798
63	8.2	0.814
64	8.2	0.789

Mean 0.808 ± 0.004

Table 3

Intensity ratio for the D-alpha line

Plate No.	Interferometer separation, mm.	Intensity ratio I(23) / I(145)
12	7.6	0.794
13	7.6	0.800
33	7.8	0.804
34	7.8	0.815
21	8.0	0.809
22	8.0	0.817
27	8.0	0.807
44	8.2	0.809
47	8.2	0.791
48	8.2	0.787

Mean 0.803 ± 0.003

7.2 Wavelengths

As mentioned before, only two main groups of components of the H-alpha line can be resolved. As far as the property of symmetry is concerned, the larger component-group (145) is superior to the smaller one (23). Therefore, the larger component group was used by Houston and by Drinkwater, Richardson and Williams in their determinations of the Rydberg constants. It was also used in this work. After properly corrected, the results of the wavelength measurements are given in tables 4 and 5.

Table 4

Wavelength of the H-alpha line

Hα Plate No.	Interferometer separation, mm.	Wavelength of the (145) line, I.A.
76	7.6094	6562.85283
73	7.8037	6562.85233
77	7.8038	6562.85422
80	8.0112	6562.85342
81	8.0112	6562.85394
64	8.1776	6562.85351

Average value = 6562.85337 ± 0.00022 I.A.

Table 5

Wavelength of the D-alpha line

D_α Plate No.	Interferometer separation, mm.	Wavelength of the (145) line, I.A.
13	7.6090	6561.06823
34	7.8033	6561.06816
22	8.0107	6561.06820
27	8.0108	6561.06802
48	8.1778	6561.06796

Average value = 6561.06811 ± 0.00005 I.A.

The above two average values give the wavelengths of the (145) component-group of H-alpha and D-alpha, respectively, under normal air conditions, i.e., in dry air at 15°C. and 760 mm. Hg.

7.3 Evaluation of the Rydberg Constants

Birge has derived a system of convenient equations[19] for the calculation of the Rydberg constants, e/m and E. In order to be consistent with other atomic constants, Birge's methods and equations were used throughout this work in calculating the values for the Rydberg constants, e/m, and E.

7.3.1 The Rydberg Constant for Hydrogen, R_H

Since the wavelength of H-alpha (145) under normal air conditions was found experimentally to be 6562.85337 ± 0.00022 I.A., its wavelength in vacuum, λ_o, can be obtained by the equation

$$\lambda_o = \lambda + \lambda (u - 1)$$

In the above equation, the refractivity, u - 1, was obtained by means of the 1939 formula of Barrell and Sears[20]. For H-alpha, it was found that

$$\lambda (u - 1) = 1.81290$$

and the wave number in vacuum

$$S(145) = 15233.06682 \pm 0.00051 \quad \text{cm}^{-1}$$

In order to obtain S_H, the wave number of the H-alpha line

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[19] R. T. Birge, Phys. Rev. 60, 766 (1941).

[20] H. Barrell and J. E. Sears, Phil. Trans. 238, 1 (1939) ; R. T. Birge, Phys. Rev. 60, 771 (1941).

in the Balmer formula, two corrections advanced by Birge[21] had to be made. They are as follows :

(1) To obtain the vacuum wave number of component 1, S(1), a correction of 0.00360 cm^{-1} was added to the value of S(145). Birge recommended the use of 0.0036 cm^{-1} for two reasons. In the first place, both Williams and Gibbs[22] and Drinkwater <u>et al</u>[23] agree that if the upper part of the microphotometer curve is used to locate its center line, component 5 has only a negligible influence and this center line lies exactly 0.0036 cm^{-1} towards the red of the component 1. Incidentally this is just the correction obtained on the simple "center of gravity" theory, when the weak component 5 is ignored. In the second place, Birge recalculated the Rydberg constants with Houston's data and found that the data were internally more consistent when 0.0036 cm^{-1} was used.

(2) In obtaining S_H, another correction of 0.07327 cm^{-1} was substracted from S(1). The method of obtaining this value is as follows. The component 1 of H-alpha comes from the transitions between the two energy levels, $2p\,^2P_{3/2}$ and $3d\,^2D_{5/2}$, of a hydrogen atom. These levels are originally the levels 2

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[21] R. T. Birge, Phys. Rev. <u>60</u>, 773 (1941).

[22] R. C. Williams and R. C. Gibbs, Phys. Rev. <u>45</u>, 491 (1934).

[23] Drinkwater, Richardson and Williams, Proc. Roy. Soc. A<u>174</u>, 164 (1940).

and 3 given in the simple Bohr's theory, which are shifted when the relativistic change of mass and the spin of the orbital electron are taken into account. The amount of the level shift is given by the formula[24],

$$\Delta T = \frac{R\alpha^2}{n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)$$

For the level $2^2P_{3/2}$, $n = 2$, $j = 3/2$, and $\Delta_1 T = R\alpha^2/64$, while for the level $3^2D_{5/2}$, $n = 3$, $j = 5/2$, and $\Delta_2 T = R\alpha^2/324$. Hence the necessary correction is

$$\Delta T = \Delta_1 T - \Delta_2 T = R\alpha^2\ 65/5184$$

Birge used $\alpha = 1/137$ and calculated the correction to be 0.07327 cm^{-1}.

After the two corrections were made, it was found that

$$S_H = 15232.99715 \pm 0.00051 \quad \mathrm{cm}^{-1}$$

The Rydberg constant for hydrogen was then given by

$$R_H = \frac{36}{5} S_H$$

$$= 109{,}677.5795 \pm 0.0037 \quad \mathrm{cm}^{-1}$$

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[24] H. E. White, Atomic Spectra (McGraw-Hill Company, New York, 1934), first edition, p. 137.

7.3.2 The Rydberg Constant for Deuterium, R_D

Starting with the wavelength of D-alpha (145), 6561.06811 ± 0.00005 I.A., and following the same procedure as above, the corresponding desired values for deuterium were found to be

$$\lambda\,(u - 1) = 1.81242$$

$$S_D = 15237.14203 \pm 0.00012 \quad \text{cm}^{-1}$$

and

$$R_D = 109{,}707.4226 \pm 0.0008 \quad \text{cm}^{-1}$$

7.3.3 The Rydberg Constant for Helium, R_{He}

The value of R_{He} was calculated from Birge's equation

$$R_{He} = \frac{36}{5}\left\{ S_H + \frac{S_D - S_H}{\frac{He^+(D-H)}{D(He^+ - H)}} \right\}$$

In this equation, H represents the atomic weight of the neutral hydrogen atom ; D, the atomic weight of the neutral deuterium atom ; He^+, the atomic weight of the ionized helium atom. The latter value is equal to the difference between the atomic weight of a neutral helium atom and that of an electron. According to Birge, the respective values are : H = 1.00813 ± 0.00001 ; D = 2.01473 ± 0.00001 ; He = 4.00389 ± 0.00007 and E = 0.0005486. The wave numbers, S_H and S_D, have been calculated in Sections 7.3.1 and 7.3.2 . From the use of these figures and Birge's equation, the Rydberg constant for helium was calculated to be

$$R_{He} = 109{,}722.2694 \pm 0.0024 \quad cm^{-1}$$

7.3.4 The Rydberg Constant for Infinite Mass, R_∞

The value of R_∞ was computed by means of the equation

$$R_\infty = \frac{36}{5} \left\{ S_H + \frac{S_D - S_H}{1 - \frac{S_D H^+}{S_H D^+}} \right\}$$

where H^+ and D^+ are the atomic weights of the nucleus of the hydrogen and the deuterium atom, respectively. The values correspond to the difference between the atomic weight of a neutral atom and that of an electron. From the above equation, it was found that

$$R_\infty = 109{,}737.3111 \pm 0.0041 \quad cm^{-1}$$

7.4 Evaluation of the Values of e/m and E

7.4.1 The Value of the Specific Electronic Charge, e/m

With the Faraday constant F taken as 9651.4 ± 1.0 e.m.u., the value of e/m was calculated by means of the formula

$$e/m = \frac{S_H F (D - H)}{H^+ D (S_D - S_H)}$$

and was found to be

$$e/m = (1.75883 \pm 0.00022) \times 10^7 \quad \text{e.m.u./gm}$$

7.4.2 The Value of the Atomic Weight of Electron, E

The value of E was calculated by means of the formula

$$E = \frac{H^+ D (S_D - S_H)}{S_H (D - H)}$$

and was found to be

$$E = (5.48740 \pm 0.00069) \times 10^{-4}$$

8. ACKNOWLEDGMENTS

The writer wishes to express his sincere gratitude to Professor I. S. Bowen, whose able guidance has made possible the completion of this work, and to Professor W. V. Houston, who initiated this research. Grateful appreciation is also hereby expressed to Professor W. R. Smythe, Professor D. M. Yost and Dr. W. E. Williams for their valuable advices. The writer is indebted to his friends at the California Institute of Technology, especially to Dr. Ralph Siu, for their generous assistance during the course of this work.

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Appendix 9.1

A Method of Cooling Hydrogen Discharge Tubes

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(Received April 30, 1943)

Experiments have been performed to cool a hydrogen discharge tube by means of rapidly evaporated liquid air. The low temperatures of liquid air resulting from such rapid evaporation were measured with a calibrated copper-constantan thermocouple. A special apparatus was constructed to determine the freezing points of the substances used for calibration. Cooling of the light source down to temperatures as low as 56°K can thus be obtained with a simple arrangement and low cost.

INTRODUCTION

IN the study of the atomic spectra of hydrogen and of other light gaseous elements, it is often necessary to cool the light source because the true structure of the lines is obscured to a great extent by the temperature motion of the light-emitting atoms. A method which is most frequently used for cooling is to immerse the discharge tube in liquid air under ordinary atmospheric pressure. Spedding, Shane, and Grace[1] even tried to cool

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[1] F. H. Spedding, C. D. Shane, and N. S. Grace, Phys. Rev. **47**, 38 (1935).

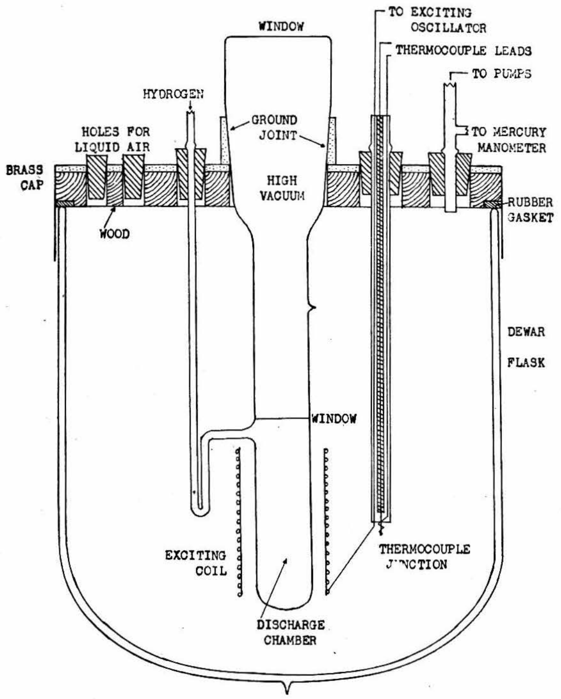

FIG. 1. Schematic diagram of the experimental arrangement for cooling hydrogen discharge tube.

their hydrogen discharge tube to still lower temperatures by means of liquid hydrogen, but this proved to be unsatisfactory.

As is commonly known, heat is required to vaporize a liquid. If the vaporizing liquid is not supplied with heat from outside it will absorb heat from the remaining liquid which will thus become cold. The faster the vaporization is going on, the colder the remaining liquid will be. Guided by this simple principle we have tried a great number of experiments to cool our hydrogen discharge tube with rapidly evaporating liquid air. To make the process adiabatic, the heat insulation of the system must be as good as possible. To make the evaporation rapid, the pumping must be fast and also the usual difficulty of leakage has to be overcome.

EXPERIMENTAL ARRANGEMENT

A schematic diagram of the experimental arrangement is shown in Fig. 1. A Dewar flask of 4.5-liter capacity is used to contain the liquid air. The open end of the flask is 15 cm in diameter and is closed with a cap made of a circular brass plate, $\frac{1}{8}$ inch thick, to which is soldered a rim of 5.5 cm in height and of $\frac{1}{2}$ mm in thickness. The cap is attached to the flask with two layers of Okonite rubber tape, which is painted with General Electric Glyptal No. 1202 to stick to the glass surface. The outside surface of the tape is further sealed with Duco cement to make it more airtight and waterproof. This has proved to be quite satisfactory. On top of the cap are the window of the light-source, inlet for hydrogen, leads to the exciting oscillator and of the thermocouple, connections to pumps and to the manometer, and holes for pouring in liquid air, which during pumping are closed with greased rubber stoppers. Two holes are provided so that the unused liquid air can be pressed out by means of compressed air blown in from one hole and a siphon inserted in the other.

The difficulty of leakage has been reduced in the following way. For glass tubes with diameter of 1.5 cm or less, they first pass through rubber stoppers of suitable size for which corresponding holes are drilled on the plate of the cap. Grease is used to improve tightness. For glass tubes with diameter larger than 1.5 cm, ground joints are used. Waxes are not so good because they crack at liquid-air temperature. Cenco vacuum pumps are used to reduce the vapor pressure above the liquid air. Pressures from 0.1 cm to 50 cm can be read on a mercury manometer.

The discharge tube consists of two parts which are separated by a glass window. The upper part is a high vacuum both for heat insulation and to prevent ice from being formed on the outside window. The lower part, the discharge chamber, is filled with hydrogen, or other gas, the atomic spectrum of which is to be studied. As pumping is going on, the level of the liquid air is gradually lowered. Therefore the discharge chamber was designed having such a length that it is always immersed in the liquid air during photographing of the spectrum. The discharge tube is excited by means of a high-frequency oscillator capable of generating electric waves ranging from 68 to 81 meters in wave-length. This method of excitation generates a very small amount of heat and does not appreciably affect the temperature of the system.

THE COPPER-CONSTANTAN THERMOCOUPLE AND ITS CALIBRATION

Giauque and his collaborators[2] have made a comparison of the copper-constantan thermocouple with the hydrogen gas thermometer from 283°K down to 10°K. Their work has proved that the copper-constantan thermocouple is suitable and satisfactory as a secondary thermometric standard at such low temperatures. Also, it is simple, convenient and compact, and has very small heat capacity. Therefore the copper-constantan thermocouple has been chosen to measure the temperature of the rapidly evaporated liquid air. For the elements of the thermocouple, No. 32 (B & S gauge) constantan wire, 70 cm long, and No. 30 enameled copper wire, 80 cm long, are used. A piece of No. 28 cotton-protected copper wire, 80 cm long, is used as the lead from the reference junction to the measuring instrument. The junctions are made by welding together the ends of the constantan and copper wires in an oxygen flame. The reference junction is always placed in a Dewar flask containing ice-water. A Rawson d.c. millivoltmeter readable to one microvolt, connected in series with a resistance box, is used to measure the thermal electromotive force.

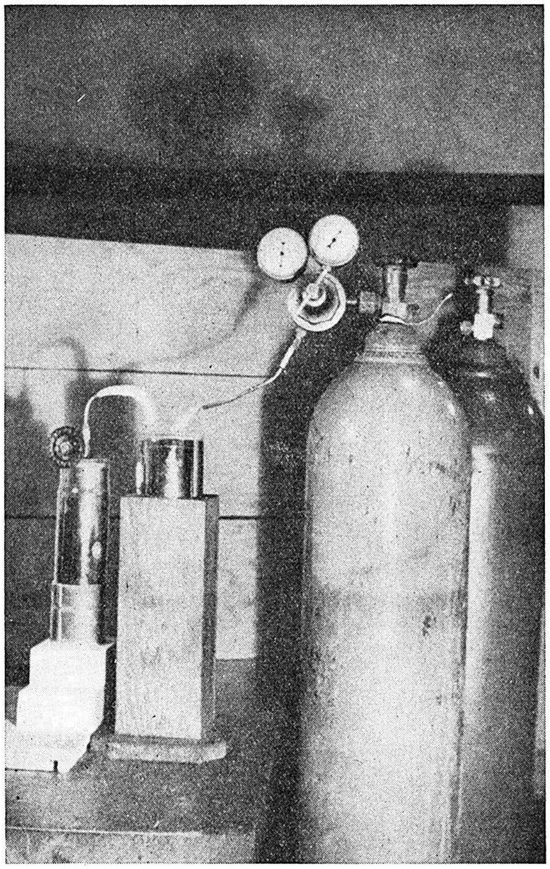

FIG. 2. Photograph of the arrangement for small scale production of liquid oxygen and nitrogen.

TABLE I.

Substance	Fixed temperature, °K	Reading, microvolts	E.m.f. from standard curve	Ratio
Melting ice	237.1	0	0	
Freezing Hg	234.2	207	1532	7.40
Freezing chloroform	209.6	336	2420	7.20
Solid CO_2 subliming under 743 mm	194.3	408	2938	7.20
Freezing toluene	178.0	487	3461	7.11
Freezing CS_2	161.5	550	3954	7.19
Freezing *n*-pentane	141.6	620	4504	7.26
Freezing isopentane	112.6	744	5208	7.00
Liquid O_2 under 748 mm	90.0	800	5681	7.10
Liquid N_2 under 748 mm	77.2	833	5916	7.10
Liquid H_2 under 737 mm	20.3	940	6618	7.04

The thermocouple was calibrated by means of the freezing points of mercury, chloroform, toluene, carbon disulfide, *n*-pentane, and isopentane, the boiling points of liquid oxygen, nitrogen, and hydrogen, and the sublimation point of solid carbon dioxide. The boiling and sublimation points were corrected to the existing atmospheric pressure by means of the formulas collected by Mueller.[3] The liquid hydrogen was made in the Cryogenic Laboratory of this institute by Professor A. Goetz. Liquid oxygen and nitrogen were made from the tank oxygen and nitrogen, in an apparatus similar to that described by Lane and Watson.[4] The arrangement for such small scale production of liquid oxygen and nitrogen is shown in Fig. 2. The results of the calibration appear in Table I.

As the freezing of a small amount of liquid is very rapid, especially when it is placed in a liquid-air bath, a special apparatus shown in Fig. 3 is used to determine the freezing points. It consists of a double-walled Pyrex glass tube,

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[2] W. F. Giauque, R. M. Buffington, and W. F. Schulze, J. Am. Chem. Soc. **49**, 2343 (1927); W. F. Giauque, H. L. Johnston, and K. K. Kelley, *Ibid.* **49**, 2367 (1927).

[3] *International Critical Tables* (McGraw-Hill Company, New York, 1926), first edition, Vol. I, p. 53.

[4] C. T. Lane and W. W. Watson, Rev. Sci. Inst. **11**, 272 (1940).

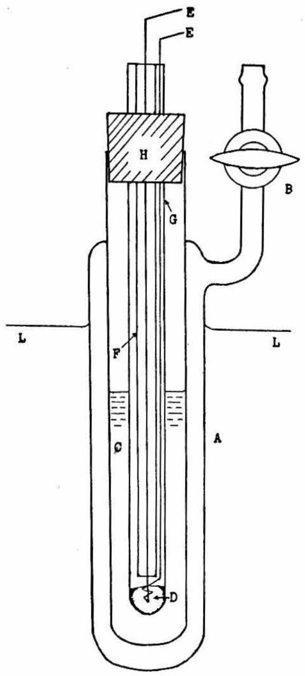

FIG. 3. Apparatus for determining the freezing point. *A*—double-walled Pyrex glass tube; *B*—stopcock; *C*—liquid to be frozen; *D*—working junction of the thermocouple with a drop of mercury for better thermal contact; *E*—thermocouple; *F*—thin rubber tube for insulation; *G*—thin glass tube (the upper ends of the thin rubber and glass tubes are waxed together); *H*—rubber stopper; *L*—level of liquid air.

3.5 cm in diameter, serving as an air jacket. The passage to the inside of the double wall is closed with a stopcock, so that the pressure of the confined air, and thus the heat insulation of the tube, can be changed. Hence the rate of cooling, or of heating, can be adjusted. In taking the cooling curve, the apparatus is immersed in a liquid air bath. In taking the heating curve, the apparatus is put in the open air. It is possible, by adjusting the pressure of the air inside the double wall, to have the freezing or melting time, during which the Rawson-meter reading keeps constant, lasting from two to ten minutes.

MEASUREMENT OF TEMPERATURE AND RESULTS

By a method similar to Adams's,[5] the data of Giauque and his collaborators,[2] giving a relation between temperature in thermodynamic scale and the thermal electromotive force of the copper-constantan thermocouple, are used to plot a standard curve, while the calibration points at the fixed temperatures are used to determine a correction or deviation curve for the thermocouple employed in this experiment. This correction curve is constructed by plotting the difference between the fixed temperature and the temperature obtained from the standard curve corresponding to the same e.m.f. value, against the voltmeter reading. In finding the temperature from a given voltmeter reading, a tentative value is first found from the standard curve. By adding to that value a correction obtained from the deviation curve, we get the corrected temperature. For example, corresponding to a reading of 889 microvolts, the tentative value of temperature is 53.6 and the correction is 2.0. Hence the corrected temperature is 55.6°K.

The usual procedure for taking a spectrogram is to pump on the liquid air at first. After the lowest temperature is reached, the oscillator is started to excite the discharge tube and the exposure of the spectroscopic plate begins. The pumping is continued until the exposure is complete. A sample of the results of cooling the hydrogen discharge tube by the use of rapidly evaporating liquid air is shown in Table II.

TABLE II.

Pressure, cm	Reading, microvolts	Time of pumping, minutes	Corrected temperature, °K
74.3	826	0	80.0
13.0	862	15	66.9
6.8	873	30	62.3
3.4	880	60	59.5
2.3	885	90	57.3
1.9	888	120	55.9
1.8	889	150	55.6
1.6	889	165	55.6
1.8	889	30*	55.6
1.9	888	45*	55.9

* After the discharge tube was started.

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[5] *International Critical Tables* (McGraw-Hill Company, New York, 1926), first edition, Vol. I, p. 57.

APPENDIX, 9.2

A Light Source for the Primary Standard of Wave-Length[*]

Despite some objections[1], the red Cd line, 6438.4696 A, still remains the primary standard of wavelength for lack of a satisfactory substitute. In our laboratory, a light source of the Michelson type has been constructed for this standard line. The interferometer spectrograms show that the line is as narrow as, or even narrower than, that emitted from the Osira Cd lamp (Adam Hilger), and is very intense. Our lamp produces a satisfactory spectrogram with only thirty minutes' exposure. Under the same conditions, the Osira lamp gives a lighter spectrogram with six hours' exposure. Furthermore, the intensity of our lamp can be varied over a wide range by changing the primary voltage of the transformer. The effective light-emitting area is 50 x 2.5 mm^2 which, if necessary, can be enlarged by means of a magnifying lens. The Doppler effect should disappear because the light is observed in a direction perpendicular to that of the current. Owing to the high intensity, simultaneous observation of the standard line and of lines from another source is possible either by using a half-reflecting mirror, or by placing the latter source in front of the spectrograph slit. These features eliminate the important objections against a light source for the standard Cd line.

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[*] Chao-Wang Hsueh, Phys. Rev. 65, 151 (1944).

[1] W. F. Meggers, Rev. Mod. Phys. 14, 59 (1942).

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