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THE PHYSICAL REVIEW.

THE REFRACTION OF GASES AT DIFFERENT TEMPERATURES AND PRESSURES.

By H. D. Ayres.

Historical.

THE greater part of the early investigations on the subject of the refraction of gases was done with one of two aims in view: (1) the determination of the constants necessary for the correction of astronomical observations, and (2) the experimental verification of the constancy of the relation $(n - 1)/\rho =$ constant, which expression is derived from theoretical considerations in the emission theory.

In general, two methods have been employed in the investigations of the subject, namely: the prism method and the interference method. Much of the early work was done by the prism method. Dulong,[1] for instance, in 1826 used a hollow prism made from a metal tube, the ends of the tube being cut at an angle to its length and closed by means of plates of glass. He used a constant deviation, that is, ran the gas into the prism until the deviation in each case was the same. Arago in his earlier work used the prism. Gladstone and Dale[2] used the prism method in the work in which they established the constancy of the relation since known under their name.

Probably the first to apply the method of interference to the problem was Arago in 1821.

Since that time various modifications of the method have been used, probably the best known of which is that due to Jamin.[3] Mascart[4]

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[1] Annales de chim. et de phys., 2 ser., t. XXXI., p. 154, 1826.

[2] Phil. Trans., p. 887, 1858; Phil. Trans., 153, 1863, pp. 317–343.

[3] Ann. de chim. et de phys., t. LII., p. 1858; t. LXI., p. 385, 1861; Comp. Rend., 1856, p. 1191; Vol. 45, 1857, p. 1892.

[4] Ann. sc. de l'Ecole Normale sup., 2 ser., t. VI., p. 9, 1877; Comp. Rend., Vol. 78, pp. 617, 679, 801, 1874; Vol. 86, pp. 321, 1182, 1878.

working with the same apparatus made some refinements and rediscussed much of the earlier work of Jamin, showing that the observations could be more nearly expressed by the relation $(n - 1)/\rho =$ const. than by the equation $(n^2 - 1)/\rho =$ const. used by Jamin.

Perreau[1] made some further modifications in the apparatus and studied the refraction and dispersion of hydrogen, carbon monoxide, and carbon dioxide, at room temperature, and pressures (differentially) to about five atmospheres.

Kayser and Runge[2] have used the prism more recently in connection with the grating.

Chappuis and Riviere[3] used a modification of Jamin's method, studying air, carbon dioxide, and cyanogen at ordinary temperature and at pressures up to 20 atmospheres. These gases were chosen because they differ widely in their densities and other physical properties. For air, the densities were computed by means of Van der Waal's equation and the constancy of the equation $(n - 1)/\rho =$ const. was found to hold within experimental errors.

For carbon dioxide, a formula from Clausius was used in computing the densities, the coefficients proposed by Sarrau being adopted. In the case of this gas a linear relation was found also.

Benoit,[4] in the course of an investigation on the comparisons of meter bars by means of the Fizeau dilatometer, had occasion to make correction for the refraction of the air. He tested the validity of the relation

$$n_1 - 1 = \frac{n_0 - 1}{760}(1 + 0.00367t)$$

by the use of his apparatus, making observations in vacuo and in air at a pressure of one atmosphere. His observations extended over a range of temperature from 0° to 80°. The results obtained verified the correctness of the expression for the pressure and temperatures used.

Apparently the only work so far published, in which the observations

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[1] Ann. chim. et de phys., (7) 7, p. 289, 1896.

[2] Ann. der Phys., Vol. 20, p. 293, 1893; Abh. der Berl. Akad., 1893.

[3] Ann. de chim. et de phys., 6 ser., Vol. 14, p. 5, 1888. (For further modifications of Jamin's principles and applications of the apparatus see: Traver's Study of Gases, Ch. XXI.; Burton, W., Roy. Soc., Proc., 80, 1908, p. 390; Magri, L., Phys. Zeitschr., *6*, 1905, p. 629; Rayleigh, Nature, 81, 1909, p. 5191; various communications to Roy. Soc., Proc. and Phil. Trans., beginning in 1904, by Cuthbertson, C.)

[4] Jour. de Phys., 2 ser., 8, p. 451, 1889. (For other work on refractivity see: Nagaoka, H., "Relation between Index of Refraction and Density," Math. and Phys. Soc., Tokyo, 2, 19, pp. 293, 1905; Rentschler, H. C., "New Method of Measuring the Index of Refraction of a Gas for Different Light-waves," Astro. Phys. Jour., 28, p. 345, 1908; Siertsema, L. H. and de Haas, M., "Refractive Indices of Gases under High Pressures," Konink. Akad. Wetensch. Ams., Proc., *14*, p. 592, 1912.

were extended to low temperatures is that of Scheel.[1] Observations were made at liquid air temperatures on atmospheric air, nitrogen, and hydrogen, at a pressure of one atmosphere, that is, readings were made in vacuo and at a pressure of one atmosphere. Assuming the correctness of the expression $(n - 1)/\rho =$ constant, Scheel deduces the values of the densities of the gases at liquid air temperatures from the refractive indices and compares the results with those obtained by other methods, and with the values computed from the gas laws. His conclusions were, that within the limits of accuracy of observation of his experiments, the constancy of the relation is established.

Other expressions have been derived in the attempt to represent more closely the relation between the refractive indices and the density, the most notable of which is probably that arrived at independently by Lorentz[2] and Lorenz[3] and known as the Lorentz-Lorenz formula. By a simple approximation it passes into the Gladstone and Dale formula, and on the whole it seems to be an open question whether this more complex formula represents the facts more closely than the simpler expression of Gladstone and Dale.

It appears that the method of arriving at the proper value of the densities may be a matter of greater importance than the small differences in these formulæ. Including the usual method of taking the density as directly proportional to the pressure we have already noted three methods of deducing the densities. Whatever question may remain as to the superiority of this expression or that, it is evident that the relation between the refractive indices and pressure is not in all cases a linear one.

Method and Apparatus.

In the experiments to be described in this paper the interference method was used, and the change ensuing in the optical path of light traversing twice, the distance between two reflecting surfaces upon admitting a gas to the space between the surfaces was determined. If one represents by k the total shift of interference bands of wave-length λ, and by n the index of refraction of the gas, then one has the relation

$$n - 1 = k\lambda/2d,$$

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[1] "Bestimmung der Brechungsexponenten von Gasen bei Zimmertemperature und bei der Temperature der flussigen Luft," Verhand. der Deutsch. Phys. Gesell., IX. Jahrg., Nr. 1, 1907.

[2] Wied. Ann., *9*, 642, 1880; *11*, 77, 1880.

[3] Jour. de Phys., 447, 1885. (For other expressions connecting refractive indices and density see: Edwards, Amer. Chem. Jour., *16*, 625, 1894; *17*, 473, 1895; Nagaoka, Math. and Phys. Soc., Tokyo, 2, 19, 293, 1905. For further concerning Gladstone and Dale's formula see: Landolt, Lieb. Ann., Suppl., *4*, 1, 1865; Sutherland, Phil. Mag., *27*, 141, 1889.)

where d is the distance in cm. between the surfaces. At a given temperature, since d is constant and k depends upon the pressure, it may be noted that values of n are obtained for corresponding values of the pressure.

The general plan of the apparatus used and also many of the details of manipulation have been described in previous articles in this journal[1] on expansion work at low temperatures. Many modifications in the apparatus were required however, and after considerable preliminary work, testing different schemes in the attempt to obtain a vessel suitable for containing the interference apparatus and which would hold at liquid air temperatures a vacuum or a gas under considerable pressure, the form of the apparatus described below was finally used.

The interference apparatus consisted of two plates, 18 mm. in diameter; one, G_B (Fig. 1) was of black astronomical glass with one face plane and polished, the other, G_0, of optical glass, both faces being plane and polished and inclined at an angle of a few minutes to each other. A hollow cylinder of quartz Q about 15 mm. in length separated the plates, thus giving an optical path of some 30 mm. with a vacuum or a slightly longer path when the gas was admitted. The adjustment of these parts in the steel chamber as first used was as follows: a brass disk of diameter slightly less than the inside diameter of the chamber had one surface cut out, leaving a thin rim around the edge within which the black plate would rest. To the under side of the disk were attached three small spiral springs of such length that when the two plates and quartz cylinder were in place, the upper surface of the top plate projected slightly above the top of the chamber. Upon inserting the plate glass cover disk, the springs were compressed and the parts were thus held snugly against each other, the upper surface of the optical glass being in contact with the lower surface of the cover disk. With this arrangement, however, the fringe system was altered by tightening one or another of the screws by which the chamber was held in place, and upon cooling to liquid air temperature the fringes became very much distorted. It was thus evident that the optical system must be kept free from contact with the side of the chamber, at least toward the lower end. In order to accomplish this, the optical glass plate G_0 was attached to the cover disk G_P by Canada balsam being placed concentrically with it. A hollow brass cylinder C of diameter slightly greater than that of the disk and having a very thin wall was made, and the springs s, s for holding the quartz cylinder and black glass in place were mounted on the lower edge of this brass shell. Also to its lower end were soldered the three phosphor bronze springs S to rest on the bottom of the chamber and thus keep

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[1] Vol. 20, p. 38, 1905; Vol. 25, p. 58, 1907, and references in these articles.

the top of the shell in contact with the plate cover disk. Since the optical glass *G* was fixed in place, it held the other parts in the center of the chamber by means of the brass shell. In this manner no contact was made with the outside chamber except through the springs, and the slight motion of the bottom of the chamber was not sufficient to cause a distortion of the fringe system through them.

But one serious trouble arose with this arrangement; at liquid air temperature the Canada balsam underwent some peculiar changes, becoming almost opaque at one temperature, or at one stage of the transitions. To remedy this, it was removed from the plates and three drops of solder placed on the outside of the brass shell very near the top to keep the optical system concentric. This arrangement proved satisfactory.

The chamber for containing the gas and interference apparatus was made from a piece of seamless steel tubing 2.2 cm. in diameter, and about 4 cm. long. Into one end of this was brazed a disk cut from a piece of strap steel, thus closing the end. Into the other end was ground a disk of plate glass G_P, the finishing being done with a very fine grade of carborundum powder. To the side of the tube was attached a piece of brass tubing for exhausting and admitting the gas. The chamber was mounted at the end of a quartz tube 18 mm. inside diameter and 23 mm. outside diameter and about 40 cm. long.

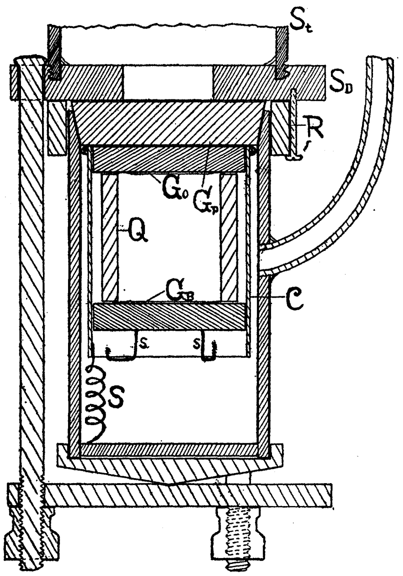

Fig. 1.

Fig. 1 is a drawing of the vertical cross section of the chamber. It shows also the plan used in attaching it to the quartz tube. A short piece of steel tubing, S_t, of diameter such that it fitted closely over the end of the quartz tube was screwed into and soldered to a steel disk S_D. The steel tube S_t was attached to the quartz tube by means of plaster of Paris.

The steel disk S_D had an opening in its center 1 cm. in diameter for admitting the light to the chamber. The lower side of the disk was ground plane and the plate cover glass G_P rested against it with stopcock grease between the surfaces. In this manner the lower end of the tube was made airtight, though it was not exhausted. In order that the chamber take a position concentric with the opening in the steel disk, a brass ring *R* was attached to the former.

The upper end of the quartz tube was set by plaster of Paris in a brass tube *B*, Fig. 2, which was rigidly attached at right angles to a brass plate. This plate was screwed to the under side of the rectangular steel block *A*. This block had leveling screws and bolts for clamping it in position after all adjustments were made.

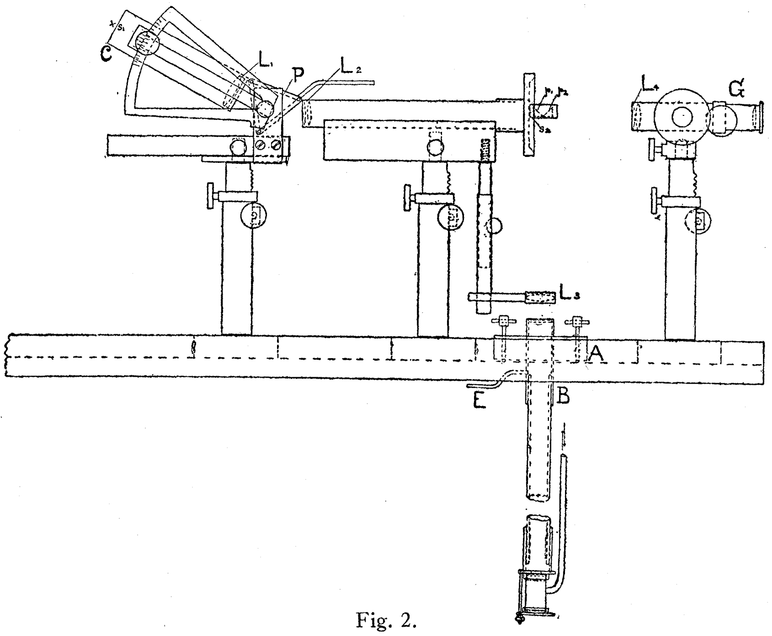

Fig. 2.

The air inclosed in the quartz tube was dry and at *E* was attached a tube with drying reagents so that, as the volume of the air in the quartz tube tended to decrease due to change in temperature, dry air was drawn in.

Fig. 2 is a side view showing the relation of the different parts of the apparatus. The whole was built on a heavy optical bench mounted at the side and about 20 cm. from the edge of a table. *C* was a collimating tube with a slit s_1 at the principal focus of the lens L_1. A flint glass prism was mounted at *P* in such a manner as to rotate upon an axis through its center. The lens L_2 brought the light to a focus at s_2, at which point was placed an adjustable spectroscope slit. The mounting of the prisms p_1 and p_2 not shown in the drawing, was such that a motion of translation in the vertical plane could be had, a rotation about an axis perpendicular to the spectroscope slit, a rotation about a second horizontal axis at right angles to this one, and finally, the whole mounting was hinged at the side and by one motion of the hand could be swung around out of the field in making other adjustments, and then brought back to exactly the same position. The light was reflected down by the prism p_1, rendered parallel by the lens L_3 which was mounted with a rack and pinion adjustment, was transmitted to the interference apparatus from which it was again reflected and again brought to a focus at the prisms and deflected horizontally by the prism p_2 to the observing telescope. This consisted of a short focus lens L_4 and a micrometer eye-piece fitted with cross hairs at right angles and double movable cross hairs. This telescope had a rack and pinion vertical adjustment and a lateral adjustment by means of a tangent screw.

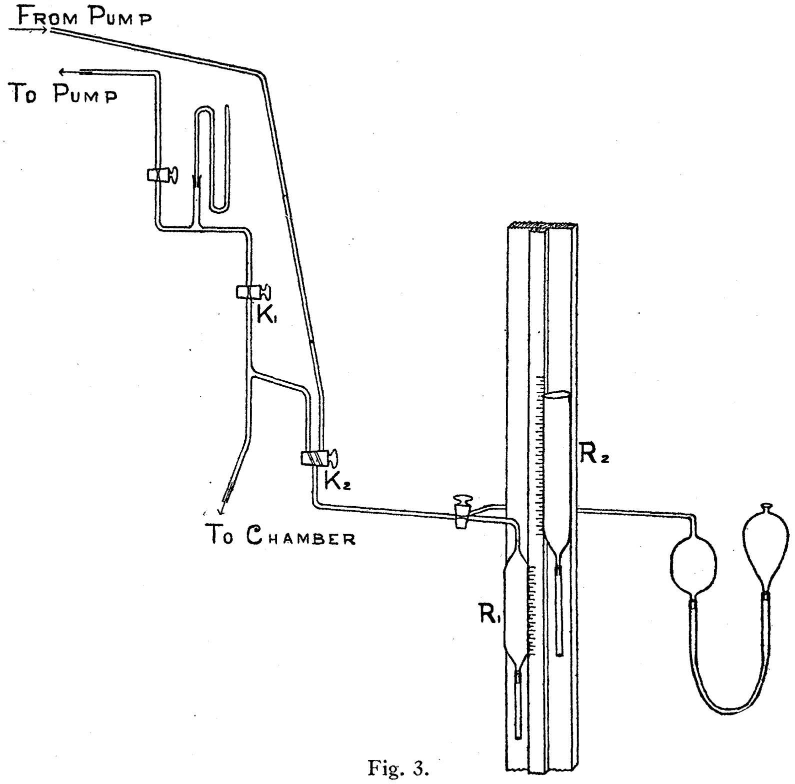

Fig. 3.

On the lower surface of the optical cover glass was cut a small circle about 1 mm. in diameter, and the fixed cross hairs in the eyepiece were set tangent to this circle. Such a circle is easily obtained by mounting the glass in the chuck of a small lathe and while rotating slowly, bring a diamond point against the surface of the glass, using a suitable rest.

The gas circuit is shown in Fig. 3. A mercury pump was placed at the side of the optical parts away from the table and connections made to it above the part of the apparatus just described. The parts shown in the diagram were mounted on the table near its end, being thus placed at the right of the optical parts, and the two principal stopcocks K_1 and K_2 were within easy reach while observing at G, Fig. 2. R_1 represents a cylindrical glass reservoir about 3 cm. in diameter and 30 cm. long; R_2 the mercury level reservoir was of the same diameter but somewhat longer. Both of these were mounted on the front side of a piece of studding extending to the ceiling. R_1 was mounted in a fixed position with its upper end a little above the top of the table.

R_2 was mounted on a carriage which could be moved up and down the timber by means of a cord passing over a system of pulleys at the ceiling. These cylinders were connected by pressure tubing which was wrapped with cord to prevent undue extension when cylinder R_2 was raised. Along the center of the timber were mounted meter bars for measuring the difference in height of the mercury columns. The readings upon these were made in a manner similar to that in reading an ordinary barometer. That is, brass collars of thin sheet brass were made of diameter a few millimeters greater than the diameter of the glass cylinders and these collars were mounted to move easily up and down over the cylinders. The lower ends of the collars were finished with pointers extending 1 or 2 mm. over the edges of the meter bars, also the lower edge of the collar and the lower edge of the pointer were in the same horizontal plane. The surfaces back of the cylinders were of such character as to give diffuse reflection. In reading, the collar was brought down until light could just be seen over the surface of the mercury, and the corresponding point on the meter bar read off. In this manner pressure readings could be made to an accuracy greater than 0.5 mm., but since the coefficient of expansion of the meter bars was not accurately known, nor to what extent, if at all, they were affected by the relative humidity, no attempt was made to read closer than 0.5 mm., and the final readings are given to the nearest mm.

In interference work where a large path difference is used, probably the most satisfactory light is the green light of the Cooper-Hewitt mercury lamp. This was used in the preliminary work, though it was the intention to use a series of spectral lines in the final observations on the gases studied. No source of light was found satisfactory for the work however, so the Cooper-Hewitt lamp was used throughout the investigation, observations being made with the green and yellow lines. The mean of the wave-lengths of the yellow lines was used in the computations.

Upon a change of pressure ensuing, it is obviously impossible to count the bands for more than one spectral line. To repeat the experiment under identical conditions and count the shift of bands for a second spectral line is also impossible. This difficulty may be overcome in two or three ways. In any case the fraction of the band nearest the fixed cross hairs is determined for each system of fringes at each pressure, *i. e.*, for the fringes of each spectral line used. Then, having counted during the change in pressure the whole number of bands moved of the wave-length chosen as the standard, the exact number including the fraction is known for this wave-length. Also the fraction of a band for the other, or for each of the other of the spectral lines used is known. If the total number of bands moved is small, the integral number corresponding to the fraction or to each of them, can usually be determined at once by inspection.

If the number of bands moved is large, and the number cannot be determined by inspection, a method similar to that given by Pulfrich[1] for the determination of the change of bands in dilatometer work by the use of two or three spectral lines instead of counting the bands may be used.

Let $a =$ the whole number of bands moved of the wave-length chosen as the standard; let $\delta_0 =$ the initial fraction, and $\delta_0' =$ the fraction after the change in pressure has taken place. Let b, δ, and δ', represent the corresponding values for a second spectral line. Then $a + \delta_0' - \delta_0 =$ the total number of bands shifted in the case of the first or standard wave-length and $b + \delta' - \delta =$ the total number of bands shifted for the second wave-length. Also

$$a + \delta_0' - \delta = N_0(1 - n_0)$$

and

$$b + \delta' - \delta = N(1 - n)$$

where N_0 and N are the total number of wave-lengths respectively in the path traversed by the light. Dividing the first equation by the second and rearranging, there is obtained

$$\frac{a + \delta_0' - \delta_0}{N_0(1 - n_0)} = \frac{b + \delta' - \delta}{N(1 - n)}$$

or

$$\frac{N}{N_0}(a + \delta_0' - \delta_0) = \frac{1 - n_0}{1 - n}(b + \delta' - \delta), \qquad (A)$$

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[1] Zeits. für Inst., 1893, p. 365.

$$\frac{N}{N_0}a = \frac{1 - n_0}{1 - n}(b + \delta' - \delta) - \frac{N}{N_0}(\delta_0' - \delta_0). \qquad (B)$$

Since $N_0 = 2d/\lambda_0$ and $N = 2d/\lambda$, one has $N/N_0 = (2d/\lambda)/(2d/\lambda_0) = \lambda_0/\lambda$ = a constant, j say. Also, for the present purpose, with a given gas the ratio $(1 - n_0)/(1 - n)$ may be considered as constant $= k$ say. Then

$$ja = k(b + \delta' - \delta) - j(\delta_0' - \delta_0)$$

or

$$\frac{j}{k}a = b + \delta' - \delta - \frac{j}{k}(\delta_0' - \delta_0). \qquad (C)$$

A table can be formed the first column of which contains the successive values of a as 1, 2, 3, etc., the second column the integral parts of the product $(j/k) \cdot a$, as 0, 1, 2, 3, etc., and the third column the fractional part of the product. The quantity $\delta' - \delta - (j/k)(\delta_0' - \delta_0)$ must correspond to the fractional part. Therefore the whole number b can be obtained from the table at once.

It is obvious that this cannot be relied upon to the same degree of accuracy as the method referred to above, which is frequently used where the interference method is applied to linear measurements only. Notwithstanding this fact, equation (C) has been found very useful in the present investigation.

A more exact though more laborious method is to solve equation (B) directly for each separate case. The only unknowns in this equation are b and n and the latter can be substituted in terms of b and N, and b thus determined.

TEMPERATURE MEASUREMENTS.

For those observations made at 0°, the apparatus was packed in powdered ice in a Dewar cylinder. Under these conditions, of course no question exists as to the constancy of the temperature nor of its absolute value. For the observations made at liquid air temperatures, a platinum resistance thermometer was used to determine the temperature. The wire of this thermometer was mounted by threading it through small holes punched in thin strips of mica, then other strips were laid on these and rolled into a ring about 3 cm. in diameter. Two leads were fused to each end of the thermometer wire. The ring was tied to the outside of the chamber. Since the chamber and thermometer were completely immersed in the liquid air it seems very probable that the temperature of the enclosed gas was that indicated by the thermometer.

The thermometer was calibrated by observing its resistance in steam, in ice, and in liquid oxygen. Callendar's formula was used, the δ being computed by means of the values of these resistances.

One series of observations was made on carbon dioxide at – 78°.3 C. This temperature was obtained by immersing the chamber in a mixture of CO_2 snow and alcohol.

It may be noted that for the observations at liquid air temperature the values of the indices obtained upon decreasing the pressure are slightly greater than those obtained upon increasing the pressure. This is due to the slight rise in temperature resulting from the evaporation of the liquid air during the progress of the readings. Except in one or two cases especially noted, this change was slight. The temperatures given at the head of the tables are the mean temperatures where the variation amounts to as much as one and one half or two tenths of a degree.

During the preliminary work on the apparatus a number of readings were made on atmospheric air, mainly at pressures of about one atmosphere. The carbon dioxide and water vapor were removed from the air. Some of the observations were made at room temperature and some at 0° C. Reducing the former to 0° and all to 76 cm. pressure by means of the relation $(n_{t,\,p} - 1)/\rho_{t,\,p} = (n_{0,\,76} - 1)/\rho_{0,\,76}$, there is obtained by taking the mean of a number of these the value 1.000 2922 for the index of refraction of the green mercury line, and 1.000 2914 for the yellow line, with a probable error of 0.000 0003. In some of these readings the pressure was obtained from roughly balanced mercury columns and may have been incorrect to 1 or 2 mm. If a corresponding series had been made when the apparatus was in its final working condition, the probable error would certainly be very much less.

The value of the index of the D-line obtained by means of a dispersion formula from the above stated values is in very good agreement with the values tabulated by Scheel.

Two or three sets of observations were also made on air at liquid air temperatures, one of which is given in the table below. The Dewar cylinder used to contain the liquid air was a poor one and the liquid air evaporated rapidly, thus causing a considerable rise in temperature during the course of the readings. The first temperature was read near the beginning and the second temperature at the conclusion of the observations.

Atmospheric Air. −189°.0, . . . − 188°.0 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
73.5	52.42	9,610	49.37	9,577
00.0	——	——	——	——
50.7	35.69	6,543	33.68	6,533
73.5	51.91	9,516	48.92	9,490
91.4	64.91	11,899	61.16	11,864
73.5	51.78	9,496	48.78	9,466

The values of the indices of air at liquid air temperature are also in good agreement with those obtained by Scheel, the only values available for comparison.

PREPARATION OF THE GASES AND OBSERVATIONS.

Hydrogen.

Aside from the numerous preliminary observations on air, the first gas studied was hydrogen. It was obtained from a cylinder of electrolytically prepared gas, and an attempt was made to remove the traces of oxygen, carbon dioxide, and water vapor. A series of observations was made at liquid air temperature, the pressure being carried only to 192 cm. of mercury. This gas was then replaced by another quantity, which was more carefully prepared. After making a large number of observations on it, in order to know definitely regarding its purity, analyses were undertaken. These were made by means of the explosion pipette. The hydrogen proved to be very impure. Whether the contamination occurred at the time of the preparation of the gas, or from a leak in the pump during several days elapsing before the analyses were made, could not be determined, but probably resulted largely from the latter cause. Some trouble at one stopcock in the pump was remedied and another quantity of gas prepared, greater care being used in its preparation.

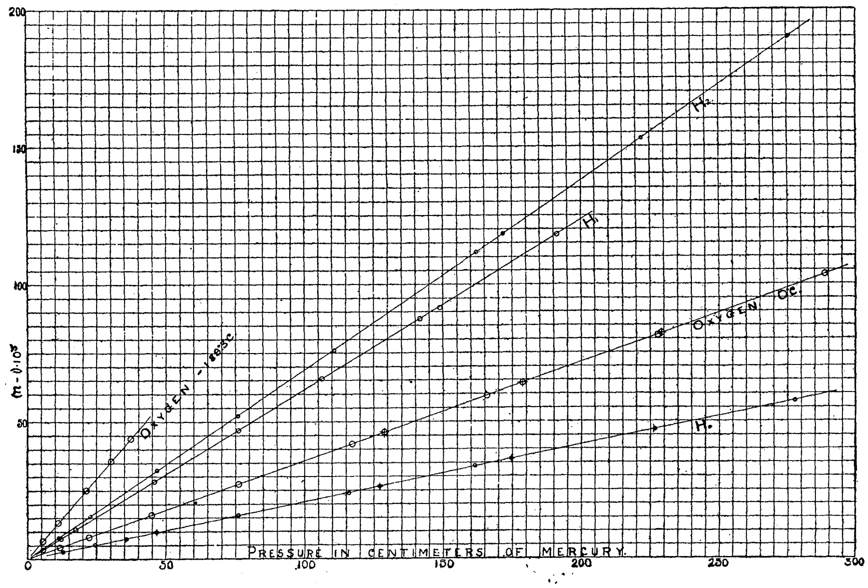

Fig. 4.

With this, one series of observations was made at − 191°.1 and one at 0°. These observations are given in the table, and the corresponding curves shown in Fig. 4. Analyses again made at the end of the work on one sample of gas drawn from the pump at the time of preparing the gas and on samples drawn at the conclusion of the observations gave the same results, and showed that this gas was also impure. The results were: hydrogen 88 per cent., oxygen 2 per cent., and though no test was made for it, the remainder in all probability was nitrogen. While it is granted that the observations on this gas are of no great value, yet since the composition of the gas is known, they may be of some interest.

Oxygen.

The oxygen also was obtained from a cylinder of the electrolytically prepared gas. Analyses of the gas drawn directly from the cylinder showed about two per cent. impurity. A test for hydrogen showed about one per cent. present. The remaining impurity was probably largely nitrogen, due to the absorbed air in the water from which the gas was made.

Because of the difficulties involved, no attempt was made to remove the trace of nitrogen, but the gas was passed over red-hot copper to remove the hydrogen, over solid caustic potash and through drying tubes including a tube immersed in liquid air. A pump was attached and the whole system of tubes containing reagents exhausted several times after allowing oxygen to enter, in an attempt to remove all traces of gases formerly contained in the tubes. The pump and gas system was also washed out with the gas previous to filling. Before the observations were begun, samples of the gas were drawn from the pump and an analysis made. Analyses were again made at the completion of the work. These were in good agreement and showed between one and two per cent. of impurity.

Two series of observations were made, one at 0° and one at − 189°.3. The observations are given in the table and the corresponding curves shown in Fig. 4. The readings at the latter temperature were continued until liquefaction began.

Nitrogen.

The nitrogen was prepared from atmospheric air by the removal of the oxygen and the carbon dioxide. Air was passed through a series of tubes containing pyrogallol, calcium chloride, lumps of phosphorus, and through phosphorus pentoxide and through a tube immersed in liquid air. Tests were made for oxygen, and it was found that a relatively large per cent. of oxygen still remained in the gas after it had passed slowly through this system. Another reservoir was then arranged so that the gas could be passed back and forth over the phosphorus and the two drying tubes. This was continued until analysis showed only a small fraction of one per cent. of oxygen. At the completion of the observations on the nitrogen, further analyses showed about the same percentage.

Three series of observations were made on nitrogen; one at 0°, and two at liquid air temperatures. At 0° the gas is well above its critical temperature, Boyle's Law is applicable, and the relation between $n - 1$ and the pressure is a linear one, or what amounts to the same thing, the relation between $n - 1$ and the density times a constant. In the case of the observations at liquid air temperatures, considerable deviation from linearity is found commencing at about one atmosphere. (See Fig. 5.) Curve (1) shows a little irregularity in the observations. The series was repeated with liquid air which had been allowed to stand for twenty-four hours, thus enabling one to work at a slightly higher temperature. These readings are shown in curve N (2). It may be noted that the observations were extended to a higher pressure before liquefaction occurred. The general form of curve is the same.

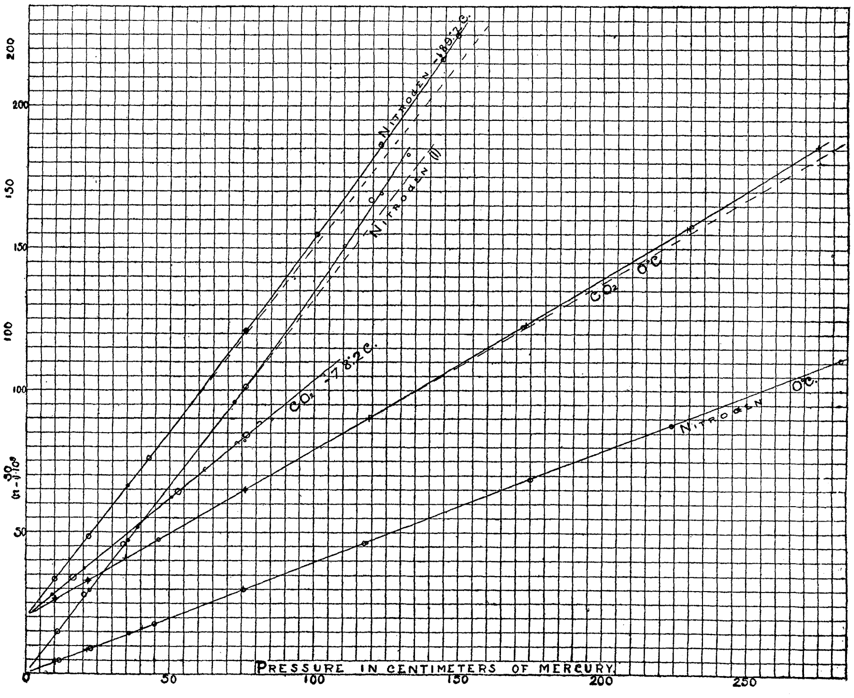

Fig. 5.

Carbon Dioxide.

Travers[1] would lead one to think that very pure gas can be obtained from the commercial product sold in steel cylinders. Acting upon this assumption, gas from a cylinder was passed through drying tubes and frozen in a tube with closed end immersed in liquid air. This tube was also connected with the pump and gas circuit, and upon closing the connection to the tube and opening that from the tube to the pump it could be exhausted to the vapor pressure of the carbon dioxide at liquid air temperature, thus removing air, etc., contained in the gas. Upon removing the tube from the liquid air and allowing its temperature to rise, the carbon dioxide would pass over into the pump and gas circuit. Analysis of the gas prepared in this manner showed about 75 per cent. carbon dioxide. An analysis of the gas direct from the cylinder showed about 95 per cent. carbon dioxide. The only explanation of this appears to be that the gas probably came from Saratoga Springs and contained one or more of the marsh gas series having a higher vapor pressure than the carbon dioxide. Consequently when the frozen mixture was removed from the liquid air, a mixture was obtained containing less carbon dioxide than the gas from the cylinder.

A Kipp generator was next set up and carbon dioxide was generated from acid on marble and purified in the same manner as that just described, except that there was added to the system of drying tubes a tube immersed in carbon dioxide snow and alcohol to remove further traces of moisture. The pump and gas system was washed with the gas as in the preceding cases. Analyses of samples of the gas thus prepared taken from the pump before the observations were begun, all showed about one half of one per cent. of impurity. In this respect the results were more satisfactory than in the case of any of the other gases.

Two series were made at 0° and one at − 78°.2. In the case of the former temperature, the circles on the curve represent the readings for one series and the crosses those for the other. It may thus be seen how closely the observations agree. Furthermore the second series was made on a different mass of gas.

For the higher pressures at 0° there is a very appreciable deviation from linearity.

In the case of the curve at − 78°.2 the readings were continued until condensation occurred, then the pressure was decreased somewhat and new readings taken, then the pressure again increased and so on. In this

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[1] Study of Gases, p. 49.

way a number of observations in that region was obtained. These are indicated in various ways in the diagram. The variation of the values is rather large, due in part to the error of observation, as some of the readings were obtained with difficulty, two thirds or more of the field being obscured by the carbon dioxide snow upon the surfaces of the glass plates. Also the pressures could not be read with great exactness under such conditions because of the changes in volume taking place.

Hydrogen (1). *—187°.5 C.*

Pressure.	Green.	
	Bands.	$(n-1)\cdot 10^7$.
5.6	1.91	350
12.0	4.09	750
17.4	5.99	1,098
45.8	15.37	2,818
106.7	35.69	6,543
141.1	47.59	8,724
191.8	64.38	11,802
149.4	49.89	9,146
76.1	25.19	4,618

Hydrogen (2). *—191°.1 C.*

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.3	4.30	788	4.02	779
22.7	8.49	1,556	8.00	1,552
46.7	17.56	3,219	16.40	3,181
76.0	28.37	5,201	26.59	5,158
110.7	41.38	7,585	38.88	7,542
162.3	60.86	11,157	57.01	11,059
171.9	64.37	11,807	60.38	11,713
222.0	83.38	15,292	78.53	15,182
275.5	103.48	18,986	97.47	18,908
221.9	83.14	15,248	78.30	15,189
171.5	64.14	11,765	60.43	11,723
122.3	45.64	8,365	42.95	8,331
75.5	28.08	5,155	26.47	5,135
36.2	13.51	2,484	12.68	2,460
5.5	2.14	392	2.02	391
11.8	4.49	823	4.19	813
23.2	8.72	1,599	8.18	1,587
31.7	11.85	2,172	11.10	2,153
76.1	28.32	5,195	26.51	5,143

Hydrogen (2). 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
12.8	1.45	266	1.29	250
24.4	2.81	515	2.62	508
35.6	4.04	741	3.76	729
76.15	8.62	1,580	8.10	1,571
116.0	13.08	2,398	12.30	2,386
162.6	18.29	3,353	17.26	3,348
226.5	25.52	4,678	24.06	4,666
277.7	31.25	5,729	29.41	5,705
226.2	25.47	4,669	24.02	4,660
174.3	19.66	3,604	18.51	3,591
127.3	14.28	2,618	13.48	2,615
76.0	8.57	1,571	8.06	1,563
46.6	5.22	957	4.96	962
25.5	2.90	532	2.76	535
0.0	—	—	—	—
28.4	3.23	592	2.99	580
76.1	8.60	1,576	8.11	1,573

Oxygen 0° C.

Pressure.	Bands (Gr.).	$(n-1)\cdot 10^7$.	Bands (Yl.).	$(n-1)\cdot 10^7$.
11.6	2.32	426	2.19	427
22.2	4.31	790	4.09	793
44.9	8.72	1,599	8.17	1,585
76.2	14.83	2,718	13.98	2,712
117.3	22.84	4,187	21.42	4,155
165.9	32.29	5,919	30.38	5,893
227.6	44.29	8,119	41.68	8,085
288.7	56.35	10,329	52.00	10,289
229.1	44.76	8,205	42.16	8,178
178.7	34.67	6,356	32.71	6,345
128.9	25.14	4,609	23.69	4,595
76.3	14.92	2,735	14.05	2,725
44.8	8.79	1,611	8.29	1,608
13.9	4.76	873	4.45	863
0.0				
76.7	14.98	2,746	14.15	2,745

Temperature, − 189°.9 C.

5.4	3.62	664		
11.0	7.24	1,327		
21.2	13.69	2,510		
30.2	19.45	3,565		
37.2	23.89	4,380		

Nitrogen. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.7	2.55	468	2.36	458
22.6	4.87	893	4.58	888
44.8	9.58	1,756	9.00	1,746
75.7	16.20	2,970	15.27	2,962
117.5	25.13	4,607	23.63	4,584
175.4	37.49	6,873	35.32	6,851
224.0	47.95	8,790	45.16	8,760
282.8	60.46	11,083	56.95	11,047
223.9	47.90	8,781	45.14	8,754
174.8	37.40	6,858	35.24	6,836
118.4	25.34	4,645	23.82	4,621
75.6	16.21	2,970	15.23	2,954
36.0	7.74	1,419	7.29	1,414
0.0	—	—	—	—
10.4	2.29	420	2.15	417
21.4	4.64	851	3.98	838
40.7	8.75	1,604	7.88	1,594
75.6	16.17	2,964	14.89	2,954

Nitrogen. − 191°.6 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.0	8.17	1,498	7.59	1,472
20.2	15.19	2,785	14.22	2,758
33.9	24.91	4,566	23.36	4,532
75.8	56.42	10,343	52.09	10,105
119.6	91.07	16,695	84.70	16,430
− 190°.6 C.				
72.6	53.21	9,754	50.20	9,738
35.6	25.67	4,706	24.18	4,691
0.0				
10.8	7.86	1,441	7.37	1,430
22.2	16.06	2,944	15.16	2,941
39.0	28.11	5,153	26.44	5,129
76.3	55.82	10,233	52.61	10,205
110.4	82.28	15,083	77.59	15,052
123.0	92.28	16,924	87.03	16,883
132.3	99.77	18,299		

Two hours elapsed between the first and second sets of the above readings.

In the curve, $N(1)$, Fig. 5, the point for the pressure of 75.8 cm. pressure in the first set should be four tenths of a division higher, and the point for the pressure of 72.6 cm. of pressure in the second set should be between three tenths and four tenths higher.

Nitrogen. – 189°.2 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$
10.1	7.27	1,333	6.81	1,321
21.9	15.72	2,882	14.82	2,875
42.8	30.49	5,589	28.71	5,569
76.4	55.09	10,099	51.87	10,062
101.0	73.60	13,493	69.35	13,453
122.8	90.69	16,625	85.45	16,576
143.5	107.08	19,629	100.87	19,567
149.5	111.81	20,497	105.45	20,458
143.4	106.98	19,611	100.83	19,560
122.8	90.50	16,590	85.32	16,551
100.9	73.48	13,470	69.29	13,441
76.2	54.77	10,040	51.64	10,018
35.5	25.19	4,618	23.74	4,605
0.0				
76.7	55.02	10,086	51.86	10,060

Carbon Dioxide. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
10.4	3.44	631	3.26	632
21.7	7.04	1,291	6.66	1,262
46.3	14.91	2,733	14.02	2,720
76.3	24.54	4,498	23.12	4,485
119.5	38.59	7,074	36.39	7,061
171.9	55.90	10,248	52.67	10,217
230.3	75.28	13,800	70.89	13,752

Series No. 2.

10.9	3.50	642	3.33	646
21.6	6.97	1,278	6.54	1,269
34.9	11.19	2,084	10.46	2,029
76.3	24.45	4,482	23.00	4,462
119.1	38.39	7,038	36.15	7,013
173.1	56.23	10,308	52.91	10 264
229.6	74.91	13,732	70.48	13,672
274.9	90.05	16,508	84.81	16,452
228.8	74.64	13,683	70.32	13,641
173.1	56.20	10,302	52.91	10,261
118.6	38.31	7,023	36.03	6,989
75.8	24.34	4,462	22.86	4,435

Carbon Dioxide. — *78°.3 C.*

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
16.6	7.53	1,380	7.10	1,377
53.0	24.10	4,418	22.74	4,411
76.6	35.10	6,434	33.06	6,413
0.0	——	——	——	——
9.3	4.23	775	3.98	772
20.6	9.33	1,710	8.78	1,703
51.0	23.04	4,224	21.72	4,213
76.1	34.53	6,330	32.49	6,303
85.4	38.13	6,990	35.97	6,978
73.4	33.33	6,110	31.40	6,091
81.1	37.25	6,829	35.07	6,803
73.0	33.27	6,099	31.39	6,089
62.4	28.48	5,221	26.80	5,199
50.7	23.09	4,233	21.75	4,219
0.0	——	——	——	——
76.1	34.01	6,235	32.02	6,211

From the various curves we have seen that within the limits of accuracy of observations of the experiments, the relation between the indices of refraction and the pressure is a linear one, except for the case of carbon dioxide at 0° and for nitrogen at liquid air temperature. In other words, the relation between the refractive indices and the density as computed by Boyle's law is a linear one.

For the carbon dioxide at 0° and the nitrogen at liquid air temperature the densities have been computed by means of van der Waal's equation. The values of the constants a and b of the equation were obtained from the critical pressure and temperature of the respective gases. For carbon dioxide the values of the critical pressure given in the tables vary rather widely. A value of 5,700 cm. of mercury was chosen, and 304° abs. as the temperature. By the use of these values were obtained, $a = 137{,}000$ and $b = 0.942$. The curve showing the relation between the resulting densities and refractive indices is given in Fig. 6. The points fall very accurately on a straight line.

The critical values of nitrogen as used were, 2,660 cm. and 146° abs. The resulting values of the constants are $a = 126{,}070$ and $b = 1.325$. The densities were computed for the pressures in the series $N(2)$. In this series the values of the pressures for increasing values and those for decreasing values are very near each other, in some cases identical. Where they are not identical the mean of the two was taken, also the corresponding mean of the indices of refraction in plotting the curve.

The curve is shown in Fig. 6. The points lie on a straight line except the last two.

In order to compare further the variation of the refractive indices with the densities as obtained by the two methods, and also to compare the formula of Gladstone and Dale with the Lorentz-Lorenz formula, the table on page 182 is given. The first column contains the pressure and the fourth the corresponding refractive indices; the second column contains the densities as obtained by Boyle's law, the third the densities as obtained by using van der Wäal's equation, the fifth the values of the constant as given by Gladstone and Dale's expression, using the values of the densities in the second column, the sixth the values of the constant as given in the third column, and the seventh and eighth columns the corresponding values of the constant of the Lorentz-Lorenz formula.

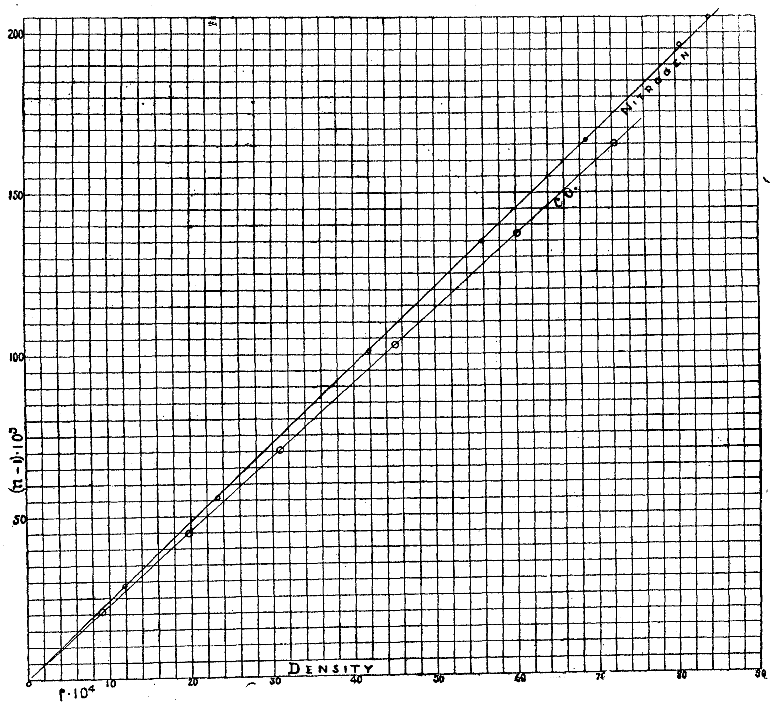

Fig. 6.

It may be noted that the variation of the values in the last column is two per cent. and the variation of those in the sixth column also two per cent.

It may be of interest to state that for nitrogen at 0° C. (excluding the two lowest pressures), computing the densities by Boyle's law and using the Gladstone and Dale expression, the values of the constant vary only about two tenths of one per cent.

Nitrogen. —189.2° C.

Pressure in Cm. Mercury.	Densities Obtained by Using Boyle's Law.	Densities Obtained by Using van der Waal's Equation.	Indices of Refraction.	Values of the Constant in Gladstone and Dale's Expression Using Densities from Column Two.	Values of Constant in Gladstone and Dale's Expression Using Densities from Column Three.	Values of the Constant in the Lorentz-Lorenz Expression Using Values of the Densities from Column Two.	Values of the Constant in the Lorentz-Lorenz Expression Using Values of the Densities from Column Three.
10.1	0.000543	0.000544	1.0001333	0.2455	0.2450	0.1637	0.1633
21.9	.001177	.001187	.0002882	.2448	.2434	.1632	.1623
42.8	.002301	.002328	.0005589	.2429	.2401	.1619	.1600
76.4	.004101	.004194	.0010099	.2462	.2408	.1641	.1605
101.0	.005424	.005589	.0013493	.2481	.2414	.1658	.1609
122.8	.006601	.006874	.0016625	.2518	.2419	.1678	.1612
143.5	.007709	.008054	.0019629	.2546	.2438	.1697	.1624
149.5	.008036	.008411	.0020497	.2551	.2437	.1699	.1623

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PHYSICAL LABORATORY,
CORNELL UNIVERSITY.