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THE INDEX OF REFRACTION OF GASES.

By Janet Tucker Howell.

A NUMBER of laws have been formulated to express the relation between the index of refraction of a substance and its density. Gladstone and Dale[1] first proposed the empirical relation

$$\frac{\mu - 1}{d} = \text{constant.}$$

This equation is the one most generally used as it holds within experimental error for the range of densities usually investigated. The most serious rival to the law of Gladstone and Dale is the relation proposed by H. A. Lorentz;[2] namely,

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = \text{constant.}$$

For gases, at low pressures, this amounts to the same thing as the law of Gladstone and Dale, since μ is so nearly equal to 1.

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = \frac{(\mu - 1)(\mu + 1)}{(\mu^2 + 2)d} = \frac{2}{3}\frac{\mu - 1}{d}.$$

But at sufficiently high pressures it should be possible to tell which law is better. This has been tried by several investigators, but with discordant results.

Mascart,[3] using an interference method, found that, for air, $\mu - 1$ increased more rapidly than the pressure.

Chappuis and Rivière[4] found that, for air and carbon dioxide, $\mu - 1$ is proportional to the density up to 20 atmospheres.

[1] Phil. Trans., p. 887, 1858; p. 317, 1863.

[2] Lorentz, Theory of Electrons, p. 143.

[3] Comptes Rendues (78), p. 617, 1874.

[4] Ann. de Chim. et de Physique (14), p. 5, 1888.

Carnazzi,[1] working with a prism, found that $(\mu - 1)/d$ increased for air and decreased for carbon dioxide as the pressure was increased.

Gale,[2] with a modification of the Jamin refractometer, found that, for air, there is no more than .1 per cent. departure from $(\mu - 1)/d$ = constant, up to 20 atmospheres.

Magri[3] measured the refractive index of air by means of a Jamin refractometer, varying the pressure from 1 to 176 atmospheres. Comparing $(\mu - 1)/d$, $(\mu^2 - 1)/d$, and $(\mu - 1)/((\mu^2 + 1)d)$, he found that the last function is the only one that remains constant.

This work was originally undertaken with the intention of investigating the effect of density on the index of refraction of several gases, up to 200 or 300 atmospheres. Owing to the difficulty of constructing a bomb for holding the interference apparatus that was capable of standing such high pressures, these experiments were delayed and the work reported here was carried out as a preliminary investigation. It is an attempt to extend the dispersion curves of several gases as far as possible into the ultra-violet, as the method employed is admirably suited to this work. This method, involving the use of a Fabry and Perot interferometer in connection with a spectroscope, has several advantages over the usual method with the Jamin refractometer for certain fields of work. The temperature can be more easily controlled, and, since it is not necessary to count the number of interference bands going by for a change of pressure of an atmosphere, it is possible to work in the ultra-violet region. Miss Matthews[4] used this method in investigating the effect of change of temperature on the index of refraction at constant pressure and found it very satisfactory.

A great deal of work has been done on the indices of refraction of gases in the visible spectrum—the most recent being that of C. and M. Cuthbertson. Using a Jamin refractometer they determined the indices of refraction of air, oxygen, nitrogen, hydrogen,[5] neon,[6] krypton, xenon, helium, and argon,[7] between λ 6563 and λ 4861.

Rentschler,[8] using a Fabry and Perot interferometer and a concave grating, determined the indices of refraction of air, nitrogen, oxygen, carbon dioxide and carbon monoxide, from λ 5769 to λ 3341. His interferometer plates were silvered and, as the reflecting power of silver is low

[1] Il Nuovo Cimento (6), p. 385, 1897.
[2] PHYS. REV. (14), p. 1, 1902.
[3] Phys. Zeitschr. (6), p. 629, 1905.
[4] Journal of the Franklin Inst., p. 673, June, 1914.
[5] Proc. Roy. Soc. (83), p. 151, 1909.
[6] Proc. Roy. Soc. (83), p. 149, 1909.
[7] Proc. Roy. Soc. (81), p. 440, 1908.
[8] Astro. Jour. (28), p. 345, 1908.

between λ 2280 and λ 3150, he was unable to extend his readings any further.

With interferometer plates nickeled by cathode discharge, and by using a Fabry and Perot interferometer in connection with a quartz spectrograph, I have been able to extend the dispersion curve of air to λ 2652 and those of hydrogen, oxygen, and carbon dioxide to λ 2753. From the values found for the indices of refraction the dispersion formulae of these gases were calculated by the method of least squares.

APPARATUS.

The apparatus is shown in Fig. 1. Light from the source *S* is focused on the quartz window *A* of the tube *H* containing the interferometer plates *C*, by means of the quartz lens *L*. The tube *H* is immersed in a constant temperature oil bath *B*. A lead pipe *M* leads to a manometer

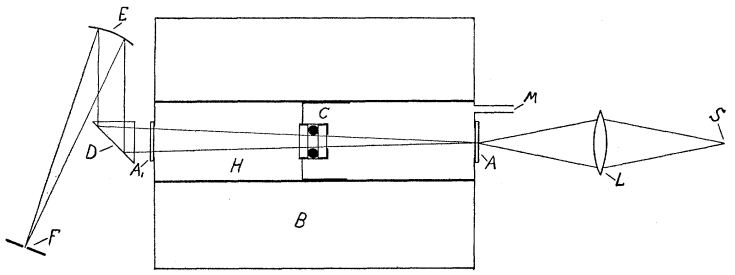

Fig. 1.

and pump so that the pressure can be changed and read. The temperature seldom varied more than .05° C. during an exposure and with air, the pressure was kept constant to within 2 mm. With the other gases it was found more difficult to regulate the pressure, but the change during an exposure was never greater than 1 cm. and usually much less. The interferometer *C* consists of two plane parallel quartz plates nickeled by cathode discharge. They are separated a constant distance *d* by an etalon so that $2d = .952$ cm. approximately. After passing through the interferometer plates, the light goes through the quartz window *A'*, is turned by the right-angled quartz prism *D* so that it falls on the concave speculum mirror *E* which brings the ring system to a focus at *F*. *F* is the slit of a Hilger quartz spectrograph, size *c*, giving a spectrum 200 mm. long from λ 2100 to λ 8000.

SOURCE OF LIGHT.

A glass helium tube was used for wave-lengths between λ 6678 and λ 3188. For shorter wave-lengths this was replaced by a quartz mercury

arc. It was found impossible to get interference bands with wave-lengths below λ 2652 with the nickeled plates used. Photographs were taken with water-cooled arcs in a vacuum as the source of light. Cd, Zn, Cu, Bi, Al, Co, Ni, Fe, Ag, Sn, Al, and brass were tried, usually with the hotter electrode brass so that it would not melt during a long exposure. Cd, Zn, Cu, Al, Sn, and brass gave some good lines for longer wave-lengths, Cd being the best, but there were no good lines below λ 2652. Therefore the idea of using a metallic arc in a vacuum was given up and the He tube and the Hg arc were used entirely.

PURITY OF GASES.

The gases used were air, oxygen, hydrogen and carbon dioxide. The oxygen was 98 per cent. to 99 per cent. pure, the hydrogen was prepared electrolytically and was 99.8 per cent. pure. Commercial carbon dioxide was used and its purity cannot be vouched for, but, as the dispersion curve found is almost identical with that of Rentschler, the purity of the gas is probably the same and the curve may be considered as an extension of his.

METHOD.

In calculating the index of refraction of any line the following procedure was used. Two exposures were taken on one plate, one at atmospheric pressure, the other with the pressure reduced almost to a vacuum. During the two exposures the temperature was kept constant. Before taking the photograph the number of whole bands going by for this change in pressure was counted for one of the visible lines. Knowing the number of whole bands going by for this line, the fraction was found in the following way:

In Fig. 2 we have the line λ 5876 at low and at atmospheric pressure. As the first two rings were always too broad to set on with accuracy, the diameters of the third to seventh rings were measured in both A and B, and, from the formula $D_2^2 - D_1^2 = (8R^2/P)$, the constant $(8R^2/P)$ was determined. D_1 and D_2 are the diameters of any two successive rings. P is the order of the ring system and R is the focal length of the concave mirror which focuses the ring system on the slit of the spectroscope. As P is of the order of magnitude of 25,000 and changes about 15 to 20 in going from the third ring at atmospheric to the seventh at low pressure, the error introduced by averaging the value of $(8R^2/P)$ from the diameters in both A and B is entirely negligible.

$$p = P_1 + P_1 \frac{x_1^2}{8}, \qquad (1)$$

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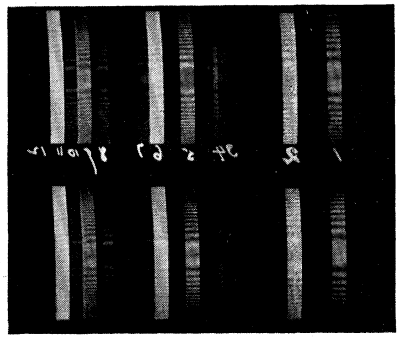


A Low Pressure.

B Atmospheric Pressure.

λ 5876

Fig. 2.

JANET TUCKER HOWELL.

where p is the order of interference at the center, P_1 is the order of the first ring, and x_1 is the angular diameter of the ring. Then the fraction of a ring that has passed the center is

$$p - P_1 = P_1 \frac{x_1^2}{8} = \frac{P_1 D_1^2}{8R^2}, \qquad (2)$$

where R is the focal length of the mirror and D_1 is the diameter of the ring of order P_1. $(8R^2/P)$ is averaged for all the rings as described above. Then measuring the diameter of the third ring and substituting in (2) we get

$$p - P_3 = 2 + \text{a fraction}.$$

And, in the same way, for each diameter we get a whole number + a fraction, the fraction being the same for all rings of photograph B. In this way, the fraction is determined for atmospheric and then for low pressure, and the difference between these two fractions (atmospheric—low) will give the fraction of a band that has gone by for the change in pressure used. The whole number has been counted visually so that the whole number + the fraction = k, the total shift in interference bands for the known change in pressure.

Then

$$\mu - 1 = \frac{k\lambda}{2d} = \frac{k}{p}.$$

d is the distance in cm. between the interferometer plates; p is the order at the center; d and λ are known, so that p can be found, and, knowing p and k, we get $\mu - 1$, where μ is the index of refraction.

This having been done for one line in the visible spectrum, values can be found for the neighboring lines and in this way the readings may be extended into the ultra-violet. The fraction is found in the same way, and the whole number can be obtained from the whole number of the line above since, with this method, very few whole bands go by and, if six is the right number, five or seven will throw the values very far off the curve. The value of the result depends entirely on the accuracy with which the fraction is determined.

The values of $\mu - 1$ are reduced to standard conditions by means of the following equation

$$(\mu - 1)_{\text{standard}} = (\mu_1 - 1)\frac{76}{p_1}\left(1 + \frac{t_1}{273}\right).$$

p_1 is the difference in pressure used to calculate μ_1 and t_1 is the temperature of the bath during the exposure.

RESULTS.

The indices of refraction of the different gases investigated are given in Table I. at 0° C. and 76 cm. pressure. The dispersion curves are shown in Figs. 3 and 4. In Table I. the wave-length given as λ 3022 is a double line λ 3021 and λ 3023.

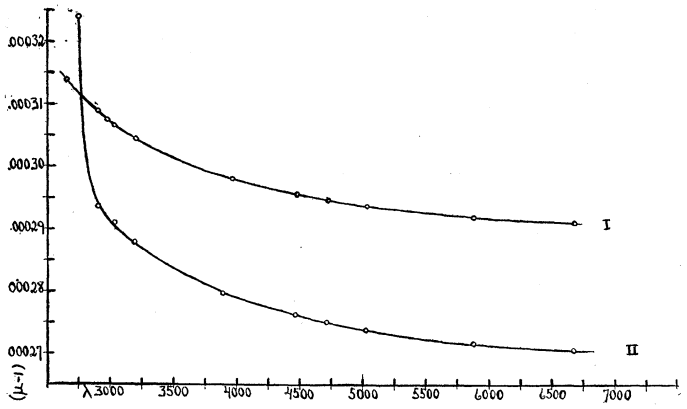


Fig. 3.

Dispersion Curves: I., Air; II., Oxygen. Abscissae: λ in Ångstrom units. Ordinates: $(\mu - 1)$.

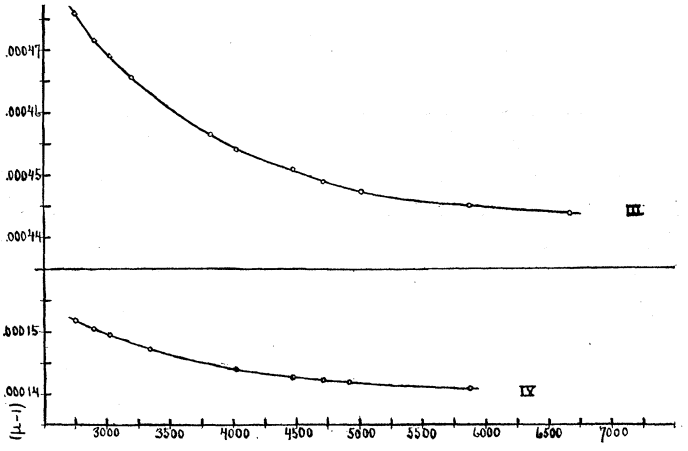


Fig. 4.

Dispersion Curves: III., Carbon Dioxide; IV., Hydrogen. Abscissæ: λ in Ångstrom units, Ordinates: $(\mu - 1)$.

DISPERSION FORMULÆ.

Air.

It has been customary to express dispersion curves in terms of the Cauchy formula

TABLE I.

λ in A. U.	Air (μ—1).	Oxygen (μ—1).	Hydrogen (μ—1).	CO_2 (μ—1).
6678 (He)	.00029120	.00027083		.00044379
5876 (He)	.00029196	.00027184	.00014105	.00044531
5016 (He)	.00029350	.00027401		.00044750
4916 (Hg)			.00014203	
4713 (He)	.00029440	.00027511	.00014238	.00044906
4471 (He)	.00029555	.00027631	.00014280	.00045119
4026 (He)			.00014440	.00045414
3965 (He)	.00029800			
3889 (He)		.00027965		
3820 (He)				.00045638
3341 (Hg)			.00014737	
3188 (He)	.00030430	.00028793		.00046549
3022 (Hg)	.00030662	.00029119	.00014973	.00046929
2967 (Hg)	.00030737			
2894 (Hg)	.00030902	.00029360	.00015061	.00047137
2753 (Hg)		.00032423	.00015187	.00047617
2652 (Hg)	.00031400			

$$\mu - 1 = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4},$$

although no theoretical importance can be attached to it. It is therefore given here so that the results can be compared with those of other observers.

Cuthbertson finds[1]

$$\mu - 1 = .00028854 + \frac{13.38}{\lambda^2\, 10^{15}} + \frac{5.0}{\lambda^4\, 10^{24}}.$$

Kayser and Runge give[2]

$$\mu - 1 = .00028787 + \frac{13.16}{\lambda^2\, 10^{15}} + \frac{3.16}{\lambda^4\, 10^{24}}.$$

Rentschler gives[3]

$$\mu - 1 = .0002903 + \frac{3.80}{\lambda^2\, 10^{15}} + \frac{1.23}{\lambda^4\, 10^{23}}.$$

As a result of this investigation the formula is found to be

$$\mu - 1 = .00028817 + \frac{11.83}{\lambda^2\, 10^{15}} + \frac{4.6}{\lambda^4\, 10^{24}},$$

which differs very little from the formula of Kayser and Runge.

The observed and calculated values are given below in Table II.

[1] Proc. Roy. Soc. (83), p. 151, 1909.
[2] Ann. d. Physik (50), p. 293, 1893.
[3] Astro. Jour. (28), p. 345, 1908.

TABLE II.

λ (A. U.).	μ—1 (Obs.).	μ—1 (Calc.).
6678	.00029120	.00029106
5876	.00029196	.00029198
5016	.00029350	.00029359
4713	.00029440	.00029444
4471	.00029555	.00029524
3965	.00029800	.00029756
3188	.00030430	.00030427
3022	.00030662	.00030663
2967	.00030737	.00030754
2894	.00030902	.00030884
2652	.00031400	.00031429

The mechanical theory of dispersion and the electrical theory for transparent media lead to the Sellmeier formula

$$\mu^2 - 1 = \Sigma \frac{D\lambda^2}{\lambda^2 - \lambda_m^2},$$

where D is a constant and λ_m is the wave-length of the free vibration of the electron. In the case of two absorption bands, one in the red and one in the violet, the formula takes the form

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2} + \frac{D_r\lambda^2}{\lambda^2 - \lambda_r^2}.$$

D_r is negative if $\lambda_r^2 > \lambda^2$. For the dispersion formula of air the values of D_v and λ_v^2 were found by using the values of the index of refraction of the wave-lengths λ 2894 and λ 2652, and substituting in

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2}.$$

$$D_v = 5.7 \times 10^{-4}.$$

$$\lambda_v^2 = .6455 \times 10^{-10}.$$

Using these constants and the values of μ for λ 6678 and λ 5876 and substituting in

$$\mu^2 - 1 = \frac{D_v\lambda^2}{\lambda^2 - \lambda_v^2} + \frac{D_r\lambda^2}{\lambda^2 - \lambda_r^2},$$

the two other constants were determined.

$$D_r = -8.067 \times 10^{-5}.$$

$$\lambda_r^2 = .10116 \times 10^{-6}.$$

So that the Sellmeier formula for air is found to be

$$\mu^2 - 1 = \frac{5.7\,\lambda^2\,10^{-4}}{\lambda^2 - .6455 \times 10^{-10}} - \frac{8.067\,\lambda^2\,10^{-5}}{\lambda^2 - .10116 \times 10^{-6}}.$$

The observed and calculated values of $\mu^2 - 1$ for the intermediate wavelengths are given in Table III.

TABLE III.

λ (A. U.).	μ^2-1 (Obs.).	μ^2-1 (Sellmeier) Calc.	μ^2-1 (Cauchy) Calc.
5016	.000 587 086	.000 587 053	.000 587 286
4713	.000 588 887	.000 588 860	.000 588 966
4471	.000 591 187	.000 590 931	.000 590 567
3965	.000 596 089	.000 595 676	.000 595 230
3188	.000 608 692	.000 609 460	.000 608 630
3022	.000 613 330	.000 613 160	.000 613 350
2967	.000 615 130	.000 615 770	.000 615 170

The agreement of the calculated with the observed values is about the same for the two formulæ. The Sellmeier formula is however the more interesting of the two on account of the theoretical value of the constants. The values of λ_v and λ_r for air cannot be taken to indicate definite absorption bands. They give the middle of regions of absorption in the red and violet, the absorption in the red being due probably to traces of water vapor.

Hydrogen.

It was found impossible to calculate the Sellmeier formula as there is no absorption band near enough to the region observed. The Cauchy formula found is

$$\mu - 1 = .000\ 138\ 76 + \frac{.8}{\lambda^2\ 10^{14}} + \frac{1.36}{\lambda^4\ 10^{24}}.$$

Cuthbertson gives[1]

$$\mu - 1 = .000\ 136\ 23\left(1 + \frac{7.61}{\lambda^2\ 10^{11}}\right)$$

$$= .000\ 136\ 23 + \frac{1.0367}{\lambda^2\ 10^{14}}.$$

The calculated and observed values are given in Table IV.

It is possible, from the dispersion curve of hydrogen, to calculate the ratio of e/E, where e is the charge on the dispersion electron and E the charge on the hydrogen ion. Rutherford in his recent atomic theory has assumed that the hydrogen atom consists of a single electron and a nucleus with one + charge. Bohr[2] has found this theory successful in explaining the laws of spectral series for hydrogen and we may assume therefore that theoretically the ratio of e/E should equal unity.

[1] Proc. Roy. Soc. (83), p. 151, 1909.

[2] Phil. Mag. (26), pp. 1, 476, 1913.

TABLE IV.

λ(A. U.)	(μ − 1) Obs.	(μ − 1) Calc.
5876	.000 141 05	.000 141 17
4916	.000 142 03	.000 142 30
4713	.000 142 38	.000 142 64
4471	.000 142 80	.000 143 10
4026	.000 144 40	.000 144 21
3341	.000 147 37	.000 147 02
3022	.000 149 73	.000 149 15
2894	.000 150 61	.000 150 25
2753	.000 151 87	.000 151 68

The method of calculating e/E is as follows. Assuming

$$\mu^2 - 1 = \frac{Ne^2}{\pi m(n_0^2 - n^2)}.$$

Then, since $\mu^2 - 1 = 2(\mu - 1)$ for gases

$$\mu - 1 = \frac{Ne^2}{2\pi m(n_0^2 - n^2)},$$

where N = no. of atoms in 1 c.c. of gas,

n = the frequency of the wave-length observed,

n_0 = the frequency of the free period of the electron,

m = the mass of the dispersion electron,

e = the charge on the dispersion electron.

Eliminating n_0^2 between two similar equations we get

$$\frac{Ne^2}{2\pi m}\left(\frac{1}{\mu_1 - 1} - \frac{1}{\mu_2 - 1}\right) = n_2^2 - n_1^2 = V^2\left[\left(\frac{1}{\lambda_2}\right)^2 - \left(\frac{1}{\lambda_1}\right)^2\right],$$

where V is the velocity of light. Therefore from two values of μ a value can be found for $Ne^2/2\pi m$. Then assuming $(e/m) = 5.1 \times 10^{17}$, we find Ne. By electrolysis

$$NE = 2.45 \times 10^{10},$$

where E = the charge on the hydrogen ion. Taking the ratio we find e/E, which theoretically should equal unity.

Campbell,[1] using Ketteler's values for the dispersion of hydrogen, found

$$\frac{e}{E} = .7.$$

Cuthbertson,[2] from his values, found

[1] Modern Electrical Theory (1st edition), p. 90.

[2] Proc. Roy. Soc. (83), p. 151, 1909.

$$\frac{e}{E} = .85.$$

From the dispersion curve of hydrogen found in this work, the following values of e/E were calculated (Table V.).

TABLE V.

λ	$\frac{e}{E}$
2753–3022	1.08
2753–3341	.95
2753–4026	.93
2753–4916	.90
2753–5875	.92
2894–3341	.93
2894–4026	.92
2894–4916	.88
2894–5876	.91
3022–3341	.85
3341–4026	.91
3341–5876	.90
4026–5876	.90
4916–5876	1.14
	Mean = .94

This value of e/E shows that the assumption that the hydrogen atom consists of a single electron and a nucleus carrying one positive charge—an assumption that is so well justified by Bohr's work[1] on spectral series—is also justified by the dispersion curve of hydrogen.

Oxygen.

The oxygen dispersion curve rises so steeply in the ultra-violet that it was impossible to find constants in the Cauchy equation to fit the shor wave-length end of the curve. The following equation fits the curve in the region of longer wave-lengths.

$$\mu - 1 = .000\ 2674 + \frac{1.2}{\lambda^2\ 10^{14}} + \frac{1.06}{\lambda^4\ 10^{23}}.$$

Cuthbertson[2] gives

$$\mu - 1 = .000\ 265\ 09\left(1 + \frac{7.33}{\lambda^2\ 10^{11}}\right)$$

$$= .000\ 265\ 09 + \frac{1.943}{\lambda^2\ 10^{14}}.$$

Rentschler gives[3]

[1] Phil. Mag. (26), pp. 1, 476, 1913.
[2] Proc. Roy. Soc. (83), p. 151, 1909.
[3] Astro. Jour. (28), p. 345, 1908.

$$\mu - 1 = .000\ 269\ 74 + \frac{3.72}{\lambda^2\ 10^{15}} + \frac{1.26}{\lambda^4\ 10^{23}}.$$

It was found impossible to derive a satisfactory Sellmeier formula from the curve. Probably the reason for this is that the dispersion is influenced by too many absorption bands to be adequately represented by a formula of two terms. The observed values and those calculated from the Cauchy equation are given in Table VI.

TABLE VI.

λ (A. U.).	(μ—1) Obs.	(μ—1) Calc.
6678	.000 270 83	.000 270 62
5876	.000 271 84	.000 271 75
5016	.000 274 01	.000 273 80
4713	.000 275 11	.000 274 95
4471	.000 276 31	.000 276 05
3889	.000 279 65	.000 279 93
3188	.000 287 93	.000 289 48
3022	.000 291 19	.000 293 22
2894	.000 293 60	.000 296 81
2753	.000 324 23	.000 301 65

Carbon Dioxide.

The dispersion curve for carbon dioxide is very flat in the region investigated so that only the Cauchy formula was calculated. The formula found is

$$\mu - 1 = .000\ 4375 + \frac{2.58}{\lambda^2\ 10^{14}} + \frac{2.3}{\lambda^4\ 10^{24}}.$$

Rentschler[1] gives

$$\mu - 1 = .000\ 449\ 04 - \frac{16.55}{\lambda^2\ 10^{15}} + \frac{4.03}{\lambda^4\ 10^{24}}.$$

The observed and calculated values are as follows (Table VII.).

SUMMARY.

The result of this work has been to extend the dispersion curves of oxygen, hydrogen and carbon dioxide to λ 2753 and the dispersion curve of air to λ 2652. In regions previously investigated these curves agree well with those of other observers.

From the hydrogen curve the calculated value of e/E, the ratio of the charge on the electron to the charge on the ion, is found to be .94. This agrees remarkably well with the theoretical value 1 which follows from

[1] Astro. Jour. (28), p. 345, 1908.

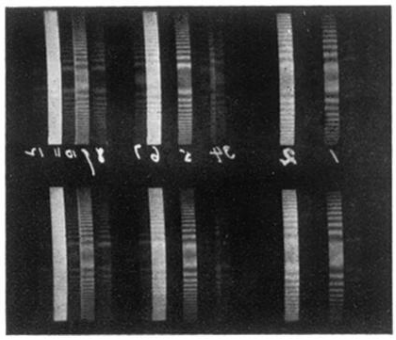
TABLE VII.

λ (A. U.).	$(\mu - 1)$ Obs.	$(\mu - 1)$ Calc.
6678	.000 443 79	.000 443 40
5876	.000 445 31	.000 445 16
5016	.000 447 50	.000 448 11
4713	.000 449 06	.000 449 58
4471	.000 451 19	.000 450 98
4026	.000 454 14	.000 454 29
3820	.000 456 38	.000 456 26
3188	.000 465 49	.000 465 32
3022	.000 469 29	.000 468 52
2894	.000 471 37	.000 471 58
2753	.000 476 17	.000 475 54

the assumptions on which the recent atomic theory of Rutherford is based. The method employed in this work is therefore found capable of very great accuracy for a small range of pressure change. Preliminary tests with large changes of pressure give indications of success in this direction although the large shift in interference bands may make it necessary to confine the work to the visible spectrum, where the whole number of bands going by can be counted.

In conclusion, I wish to thank Dr. James Barnes, at whose suggestion and under whose direction this investigation is being carried out, for the help and advice he has given me and the interest he has taken in the work.

BRYN MAWR COLLEGE,
BRYN MAWR, PA.



A Low Pressure.

B Atmospheric Pressure.

λ 5876

Fig. 2.