On the Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia

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I. *On the Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia.*

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It has long been well known that the refractive indices of simple gaseous compounds do not obey the additive law so closely as those of solids or liquids. From the study of these last Gladstone and Dale, and their followers, succeeded in obtaining refraction equivalents for a large number of the elements which were fairly constant for the same class of compound. But in gases the discrepancies were found to be

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much wider, and this appeared the more surprising since, in other fields of research, the gaseous state has proved peculiarly favourable for the discovery of simple relations.

Accumulation of Data.—The investigation, of which the present paper forms part, was designed to throw light on the cause of these anomalies.

The first step was to enlarge the field of the enquiry by the accumulation of *data*, and with this object we have, either together or in collaboration with others, determined and redetermined the refraction and dispersion in the gaseous state of fourteen elements and ten compounds within the limits of the visible spectrum, and the refraction of six elements and four compounds for a single wave-length.

The number is still far too small. Many interesting compounds remain to be investigated. But, as the present instalment of work has occupied nearly two years and has led to certain definite conclusions, it seems better to publish it rather than to await the addition of more difficult and, perhaps, less instructive examples.

Choice of Compounds.—In selecting the compounds to be examined we have been guided by the principle that the molecule should consist of as few atoms as possible, and that the refraction and dispersion of each constituent should be measurable in the gaseous state. It is unfortunate that the list of compounds which comply with these requirements is very short. All compounds of carbon are excluded. Of those substances which are dealt with in the present paper, the most important are the halogen acids, which form a regular series of simple diatomic molecules. Steam, SO_2, and H_2S form an interesting cycle, and the two oxides of nitrogen are very instructive since the constituents are the same in both cases.* Ozone is remarkable as an example of the effect of polymerization on the refractivity.

Expression of Results.—The choice of a formula for the expression of results is of fundamental importance. Previous workers on the subject of gaseous refractivities have almost invariably used that of CAUCHY, with two terms or three, according to the degree of accuracy of their figures. But this formula is not based on modern physical theory. Moreover, we have shown in a previous paper† that, when only two constants are used, it is inadequate to express the experimental results, even in the visible spectrum; while if a third constant and term involving $1/\lambda^4$ is introduced, the shape of the dispersion curve cannot be easily grasped on inspection of the figures. For these reasons we have abandoned this formula, and have used, tentatively, a formula of SELLMEYER's type, $\frac{\mu^2-1}{2} = \mu-1$ (approximately) $= \frac{N}{n_0{}^2-n^2}$.

It is unnecessary to defend the adoption for gaseous indices of this expression, which has been widely used for solids, and is in general outline established on theory

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* The examination of NO_2 and N_2O_4 has been postponed on account of its difficulty, but promises to be no less interesting and important owing to the association which characterises it.

† "On the Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen and their Relations," C. and M. CUTHBERTSON, 'Roy. Soc. Proc.,' A, vol. 83, p. 151, 1909.

and confirmed by experiment. But it is desirable to emphasise the fact that the calculation of the constants given in this paper from a formula containing only one term on the right-hand side is only provisional, since the main conclusion of the authors is that, both for elements and compounds, a single term is inadequate, except in the case of monatomic gases. The simple form of the formula is, however, useful for indicating at a glance the direction and magnitude of the changes in refractive and dispersive power which take place when elements combine to form a compound.

If μ_1 μ_2 are the refractive indices of a substance for two wave-lengths for which the frequencies are n_1 n_2, we have

$$\frac{\mu_1-\mu_2}{\mu_1-1} = \frac{n_1^2-n_2^2}{n_0^2-n_2^2} = \frac{n_1^2-n_2^2}{n_0^2} \text{ approximately,}$$

since n_2^2 is usually small compared with n_0^2. The left side of the equation expresses the dispersive power of the substance, which is thus seen to be inversely proportional to n_0^2.

Changes of Refractive Power.—Let $\mu_A-1 = \dfrac{N_A}{n_0{}^2{}_A-n^2}$; $\mu_B-1 = \dfrac{N_B}{n_0{}^2{}_B-n^2}$ be the formulæ which express the refractivity of two gaseous elements in the region of the visible spectrum, and let $\mu_{AB}-1 = \dfrac{N_{AB}}{n_0{}^2{}_{AB}-n^2}$ express the refractivity of the compound which they form. If the molecules of the two elements are diatomic, and one molecule of the compound is formed of one atom of each, then the change of refractive power on combination is

$$\tfrac{1}{2}\left\{\frac{N_A}{n_0{}^2{}_A-n^2}+\frac{N_B}{n_0{}^2{}_B-n^2}\right\}-\frac{N_{AB}}{n_0{}^2{}_{AB}-n^2}.$$

Changes of Dispersive Power.—If the additive law were strictly followed the dispersive power of a compound, measured in a region remote from free frequencies, would lie between the dispersive powers of its constituents, *i.e.*, $n_0{}^2{}_{AB}$ would lie between $n_0{}^2{}_A$ and $n_0{}^2{}_B$. For it can be shown that, for a short region of the spectrum, remote from free frequencies, so that n_0^2 is large compared with n^2 and n^4/n_0^6 can be neglected,

$$n_0{}^2{}_{AB} = \left(\frac{N_A}{n_0{}^2{}_A}+\frac{N_B}{n_0{}^2{}_B}\right)\Big/\left(\frac{N_A}{n_0{}^4{}_A}+\frac{N_B}{n_0{}^4{}_B}\right),$$

and this expression lies between these limits.

Hence, if the experimental value of $n_0{}^2{}_{AB}$ differs from this value, the variation must be due to the changes in one or more of the four quantities N_A, N_B, $n_0{}^2{}_A$, $n_0{}^2{}_B$ consequent on combination. It is evident that all four unknown quantities cannot be determined from a knowledge of N_{AB}, $n_0{}^2{}_{AB}$, which is all we obtain from a determination of the dispersion of the compound. But two cases should be distinguished. The value of $n_0{}^2{}_{AB}$ may vary owing to changes in $n_0{}^2{}_A$ and $n_0{}^2{}_B$ consequent on combination, *i.e.*, to real modifications of the free periods of the vibrators; or it may be due to the introduction of a new free period, or the elimination of an old one, previously wrapped up in $n_0{}^2{}_A$ and $n_0{}^2{}_B$.

Summary of Results.—Before proceeding to give the experimental work it will be convenient to summarise the results obtained :—

(1) In hydrochloric, hydrobromic, hydriodic acids, sulphur dioxide* and sulphuretted hydrogen* the refractivity of the compound is less than the sum of the refractivities of the elements, and the dispersive power of the compound lies between those of its constituents ;

(2) In nitrous oxide, nitric oxide, ammonia, and ozone the refractivity of the compound is greater than the sum of those of its constituents, and the dispersive power is greater than that of either constituent ;

(3) In steam the refractivity of the compound is less, and the dispersive power greater, than those of its constituents ;

(4) In all cases the change in dispersive power is great relatively to the change in refractive power.

We have framed a hypothesis which, in our opinion, would account for these changes in a qualitative manner, and we hope to publish it elsewhere.

CHLORINE.

Previous Work.—The refractive index of gaseous chlorine has only been measured twice. DULONG† found $\mu-1 = {\cdot}000772$ for white light with gas, prepared from MnO_2, whose density was 2·47 (air 1).

MASCART‡ found $\mu-1 = {\cdot}000768$ for white light. He worked at low pressures at the temperature 12° C. and compared the refractivity with that of air under the same conditions.

The dispersion of the gas has not previously been measured.

Preparation.—The gas we used was prepared by dropping strong hydrochloric acid on potassium permanganate. After washing in water and drying by sulphuric acid it was condensed in a bath of acetone cooled with solid CO_2 and then allowed to boil off till all the air in the connecting tubes had been displaced. The refractometer tube, previously evacuated, was then placed in connection with the chlorine by a capillary tube so fine that the gas entered the tube sufficiently slowly for the interference bands to be counted. When the pressure of gas in the refractometer reached that of the atmosphere the bands came to rest, and the pressure and temperature were read.

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* The figures for SO_2 and H_2S were published in 'Roy. Soc. Proc.,' A, vol. 81, p. 171, 1909.

† DULONG, 'Ann. de Chim. et de Phys.,' vol. 31, p. 154, 1826.

‡ 'C. R.,' p. 321, 1878.

After each experiment was over the gas was absorbed over soda lime and only experiments in which the impurities were negligible were used in determining the refractive index.

The light used was that of the green mercury line, $\lambda = 5461$.

Refractivity.—The following figures were obtained in five experiments, the experimental values being reduced to 0° C. and 760 mm. by the formula :—

$$\mu - 1 = (\nu - 1)\,\frac{\mathrm{T}}{273}\cdot\frac{760}{\mathrm{P}},$$

$(\mu-1)10^7$ . . . . 7976, 7985, 7966, 7986, 7981. Mean 7980.

Standard Conditions.—The practice of reducing observations of refractivity to the standard temperature of 0° C. and the pressure of 760 mm., dates from a time when deviations from the laws of BOYLE and GAY-LUSSAC were alike unknown. As accuracy improved and the field of research was extended to vapours, these *criteria* became insufficient and sometimes meaningless. MASCART, the volume of whose work entitles him to be considered the leading authority on the subject, at first adopted the old conditions, and even in the case of SO_2 expressed the refractivity as it would be at 0° and 760 mm. But, in his later work, when dealing with chlorine and bromine and with some organic compounds for which the coefficients of thermal expansion and compressibility were unknown, he contented himself with determining the refractivity at pressures as low as possible and comparing it with that of air at the same temperature (12° C).*

LE ROUX, in his experiments on sulphur, mercury, phosphorus and arsenic, expressed the ratio of the refractivity to the density, and LORENZ and PRYTZ adopted the same system. It is evident that this principle is the most convenient for those who wish to compare the refractivity of equal numbers of atoms of different elements, or of molecules of different compounds. Accordingly, in the present work, we have reduced all refractivities to the values which they would have had if the gas or vapour had the density of hydrogen at 0° C. and 76 cm., ($\cdot 000089849$) gr./(cm.)^3 multiplied by the ratio of the theoretical molecular weight of the substance in question to that of hydrogen. But, in order to avoid confusion, we shall denote this value by the symbol $(\mu-1)\,\dfrac{\mathrm{D}}{(d_{076})}$, where D denotes the standard density as here defined, and (d_{076}) the density at 0° C. and 76 cm.

The density of chlorine at the temperature and pressure of the atmosphere has been determined recently by TREADWELL and CHRISTIE.† They found that at 20° C., the molecular volume was 22039 and 22030·0 at 10° C.

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* MASCART, 'C. R.,' vol. 86, pp. 321 and 1182.

† F. P. TREADWELL and W. A. K. CHRISTIE, 'Zeits. anorg. Chem.,' vol. 47, p. 446, 1906.

The average temperature of our experiments was 19°·4 C. and at that temperature the molecular volume of chlorine would be 22038·9 c.c. That of hydrogen is 22428·8 c.c. Hence the refractivity observed must be multiplied by the ratio of these numbers. We thus arrive at the number ·00078412; and since the accuracy of the experiments is not greater than 1 part in 1000 we may accept ·000784 as the refractivity of chlorine for the green mercury line.

Dispersion.—Assuming this value, the dispersion was measured at seven other points of the visible spectrum by the method described in previous papers.*

The following table shows the results :—

TABLE I.—Dispersion of Chlorine.

$\lambda \times 10^8$.	$(\mu - 1)\, 10^8 . \frac{D}{(d_{076})}$.		
	Observed.	Calculated.	Difference.
6707·85	77563	77556	− 7
6438·5	77703	77697	− 6
5790·5	78121	78123	+ 2
5769·5	78135	78139	+ 4
5460·7	78400	78402	+ 2
5209·1	78651	78655	+ 4
5085·8	78791	78792	+ 1
4799·9	79166	79156	−10

The numbers shown in the column headed "calculated" are derived from the formula

$$(\mu - 1)\,\frac{D}{(d_{076})} = \frac{7{\cdot}3131 \times 10^{27}}{9629{\cdot}4 \times 10^{27} - n^2},$$

where n is the frequency of the light, *i.e.*, $= \frac{V}{\lambda} = \frac{3 \times 10^{10}}{\lambda \text{ (in cm.)}}$.

Relation of Dispersion to Absorption.—The absorption spectrum of chlorine has been fully investigated by Mrs. LAIRD.† She describes the spectrum as consisting of (1) a region of general absorption which extends, in a column of gas 60 cm. long, from λ 4650 to λ 2599, and lengthens in both directions with increasing pressure, but chiefly towards the less refrangible end, reaching λ 4990 at $2\frac{1}{2}$ atmospheres; and (2) a line spectrum lying between λ 4799 and λ 5350 which consists of groups of dark lines, giving a fluted appearance to the eye. With increased pressure these lines became more intense but did not increase in numbers where they had been visible before. In addition there may be patches of general absorption in the region of line spectrum.

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* See 'Roy. Soc. Proc.,' vol. 83, p. 152, 1909.

† 'Astrophys. Journal,' 14, p. 85, 1901.

The region of which the refractivity was measured by us extended from λ 6708 to λ 4799·9 and thus covers the whole range of the line spectrum and 200 Å.U. which are affected by the general absorption.

It is, therefore, of interest to find that the observed values of the refractivity lie on a smooth curve. But it is significant that the calculated curve cuts across the experimental, in which the curvature is greater. This appears to indicate that a single term formula is inadequate to express the results, and that a second term is required, in which both N and n_0^2 are small, to represent the influence of the absorption band.

In the region of the line spectrum it was to be expected that if any variations of refractive index accompanied the variations of absorption they would be found either in the immediate neighbourhood of each dark line or possibly affecting the whole breadth of each group of lines forming a fluting. In order to investigate this point the following test was made:—

The paths of the two interfering rays of light were equalised, so that when the wave-length of the light employed was continuously changed from red to violet no change was observed in the position of the interference bands in the field of view. Chlorine was then admitted into one tube till the path of that beam had been retarded by 450 bands ($\lambda = 5461$). Next, by means of the compensator,* the same beam was accelerated by an equal amount. If, now, the wave-length of the light be changed from red to violet any movement of the bands would be due to the difference of refractivity of glass and chlorine for the particular wave-length which is in the field of view. The bands can easily be read to 1/10, so that when 450 bands have passed a difference of refractivity of 1/4500 can be detected.

The slit was then narrowed till the interference systems due to λ 5790 and λ 5769 were clearly separated in the field of view: *i.e.*, till the light composing any particular part of the image varied by less than 20 Å.U. On changing the wave-length continuously from red to violet no sudden change in the bands could be detected. It may therefore be concluded that between λ 6708 and λ 4799 any sudden change of refractivity exceeding $\cdot000784/4500 = \cdot0000017$ must be confined to a breadth of less than 20 Å.U. and probably to less than half that amount. It is not possible to detect small changes in the refractivity in a narrower section of the spectrum than this, since, if the light is sufficiently dispersed, it becomes too feeble to read tenths of a band.

BROMINE.

Previous Work.—DUFET records MASCART'S value $\mu = 1\cdot001125$ for the D line. The dispersion of the gas has, apparently, not been attempted.

Preparation.—The purest bromine obtainable from Kahlbaum was used. Before every experiment the bulb containing the liquid was cooled to −80° C. and exhausted,

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* This compensator, of special construction, retards all wave-lengths equally except in so far as dispersion affects them.

so as to get rid of traces of HBr which might have formed since the previous experiment. Since it was necessary for the gas to pass through greased taps more elaborate precautions for purification would have been useless. The grease used was specially prepared from pure paraffin wax and oil. After each experiment the vapour which entered the refractometer tube was admitted to contact with the mercury and absorbed. Any admixture of HBr would have been measurable as hydrogen. In the experiments on which we rely to obtain the index the residue was negligible.

Procedure.—In order to reduce the observed refractivity to standard conditions it was necessary to measure the density of vapour employed. For this purpose the bulb containing the liquid was connected with a density bulb in parallel with the refractometer tube and a determination of the density of the vapour accompanied each experiment. The atomic weight of bromine was taken as 79·97 (O = 16). Owing to the great absorption of the vapour in the green it was necessary to use red light for the determination of the absolute index. With λ = 6438 as many as 80 or 90 bands could be read, whereas at λ 5461 the band system was no longer readable after 25 bands had passed.

The absolute index was determined from the following five experiments which were well corroborated by several others not quite so trustworthy :—

TABLE II.—Refractive Index of gaseous Bromine, λ = 6438.

Experiment.	$(\mu - 1)\,10^6\,\frac{D}{(d_0 76)}$.	Number of bands counted.
1	1158	55
2	1156	65
3	1154	89
4	1159	50
5	1157	80
Mean	1157	

Dispersion.—Owing to the strong absorption of the vapour in the visible region measurements of the dispersion were difficult, and the accuracy attained was much inferior to that shown in the case of chlorine. The following figures show approximately the number of bands which were readable at different points of the spectrum :—

$\lambda \times 10^8$.	Number of bands readable.
6708	More than 120.
6438	„ „ 120.
6000	„ „ 115.
5700	Less „ 90.
5650	„ „ 60.

$\lambda \times 10^8$.	Number of bands readable.
5600	Less than 30.
5461	„ „ 25.
5209	„ „ 20.
5085	„ „ 10.

Beyond 5461 the number of bands read was not sufficient to ensure trustworthy values.

The following table gives the experimental values in column 2 :—

TABLE III.—Dispersion of gaseous Bromine.

$\lambda \times 10^8$.	$(\mu - 1)\,10^7 \dfrac{D}{(d_0 76)}$.		
	Observed.	Calculated.	Difference.
6708	11525	11518	− 7
6438	11570	11571	+ 1
6000	11662	11675	+ 13
5800	11735	11731	− 4
5750	11741	11746	+ 5
5700	11762	11762	0
5600	11796	11767	− 29
5461	11849	11842	− 7

The experimental numbers fall approximately on a smooth curve which is given by

$$(\mu-1)\,\frac{D}{(d_0 76)} = \frac{4{\cdot}2838 \times 10^{27}}{3919{\cdot}2 \times 10^{27} - n^2}.$$

The figures calculated from this equation are given in column 3.

Relation of Dispersion to Absorption.—As in the case of chlorine a test was made for a rapid change of refractivity affecting a narrow section of the spectrum, but none was detected.

In this case also the change of refractivity is small compared with the increase of the absorption as we pass from the red to the green.

IODINE.

Previous Measurements.—The only determination of the refractive index of iodine on record is that of HURION,* who gives $\mu = 1{\cdot}00205$ for the red and $1{\cdot}00192$ for the violet. He employed a prism and heated the iodine to 700° C.

It was hoped that with a refractometer a higher degree of accuracy could be obtained, but the results of experiment were disappointing. The absorption band which has its maximum at λ 5000 extends so far into the red that, with the faint light available in a Jamin apparatus, the band system was very soon obliterated.

In the red (λ = 6438) as many as 21 bands could be observed with difficulty, but

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* 'Journal de Physique,' I., VII., p. 181.

at λ = 5600 it was not possible to read more than three, and on the violet side of the region of absorption no measurements were possible. In attempting to measure the dispersion the experimenter has to choose between a small number of bands read over a slightly wider range and a larger number read over a small range. In either case the errors of observation are relatively large.

Procedure.—A weighed quantity of iodine was introduced into the refractometer tube which was evacuated and sealed off.*

The tube was then heated till the solid had all sublimed and the bands observed.

Refraction.—The wave-length selected for the absolute determination was 6438, and this was obtained from white light of a Nernst lamp by means of a fixed deviation spectroscope. The volume of the refractometer tube was 49·1 c.c. and the weight of iodine which it contained was ·00473.

The best experiments gave for $\mu-1$ the value ·00210, and this is probably correct to 1 or 2 per cent. It agrees well with HURION's value, which was probably for a longer wave-length than 6438.

Dispersion.—Assuming this value the following numbers were obtained for the refractivity in the red-orange, the number of bands read being 9·7 for λ = 6438.

TABLE IV.—Dispersion of gaseous Iodine.

$\lambda \times 10^8$.	$(\mu-1)\,10^6\,\dfrac{D}{(d_0 76)}$.
6438	2100
6280	2100
6150	2150
6100	2180, 2170, 2140

In another set of readings the number of bands read was only 2·1 in the red, and the following readings were taken :—

$\lambda \times 10^8$ . .	6708,	6438,	6215,	6180,	5600,	5250,	5100,	5005,	5000.
$(\mu-1)\,10^6$.	1970,	2100,	2130,	2130,	2170,	2250,	2210,	2160,	2120.

These numbers are, of course, of little individual value, but they show at least the order of magnitude of the variation of refractivity in passing through an absorption band. The last set is interesting in showing the fall of index which seems to occur a little on the red side of the region of greatest absorption.

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* The method is more fully described in a previous paper by one of us (see 'Phil. Trans.,' A, vol. 204, p. 323, 1905).

It was not considered worth while to spend further time in multiplying observations which could never command great confidence, owing to the fewness of the bands read. We hope to return to this element, using the method of crossed prisms, which is more suitable than that of the interferometer.

Hydrochloric Acid.

Previous Determinations.—Dulong obtained 1·000447 for white light, and Mascart 1·000444 for the D line. The dispersion has never before been attempted.

Preparation.—The gas was prepared by dropping sulphuric acid on pure sodium chloride. After passing through two drying bulbs filled with sulphuric acid it was condensed in liquid air and allowed to boil off. When the gas had flowed through the connecting tubes for 15 minutes so as to displace the air, it was admitted to the refractometer and allowed to flow till the pressure was atmospheric. The following table gives the experimental values found, reduced to 0° C. and 760 mm. by the formula

$$\mu-1=(\nu-1)\,.\,\frac{\mathrm{T}\times 760}{273\times p}\,.$$

Experiment .	1,	2,	3,	4,	5,	6,	7.
$(\mu-1)\,10^7$ . .	4514,	4513,	4508,	4512,	4510,	4509,	4510.

Mean 4511.

This value requires correction for the density of the gas. Gray and Burt* found that the volume of hydrogen from two volumes of hydrochloric acid is 1·0079.

Leduc gives the mean coefficient of expansion of the gas at constant pressure as ·003736.

The average temperature of our experiment was 16° C.

Hence the experimental value must be multiplied by

$$\frac{1\times(1+16\times{\cdot}003736)}{1{\cdot}0079\times(1+16\times{\cdot}00366)},$$

whence we obtain

$$(\mu_{5461}-1)\,\frac{\mathrm{D}}{(d_0 76)}={\cdot}000448.$$

Dispersion.—Assuming this value the dispersion was determined from six experiments. The following table shows the results:—

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* 'Trans. Chemical Society,' 95, II. of 1909, p. 1654.

TABLE V.—Dispersion of Hydrochloric Acid.

$\lambda\times10^8$.	$(\mu-1)\times10^8\frac{D}{(d_0 76)}$.		
	Observed.	Calculated.	Difference, 3 − 2.
6707·85	44375	44367	− 8
6438·5	44444	44437	− 7
5790·5	44656	44661	+ 5
5769·5	44666	44670	+ 4
5460·7	44800	44803	+ 3
5209·1	44930	44933	+ 3
5085·8	45007	44994	− 13
4799·9	45187	45191	+ 4

Using the SELLMEYER form of equation the refractivity is expressed by

$$(\mu-1)\frac{D}{(d_0 76)}=\frac{4\cdot6425\times10^{27}}{10664\times10^{27}-n^2}.$$

The values calculated from this expression, in which the constants are calculated from the observations by the method of least squares, are shown in column 3 above, and the differences between columns 3 and 2 are given in column 4.

HYDROBROMIC ACID.

Previous Determinations.—MASCART obtained $\mu-1$ = ·000570 for the D line. The dispersion has not been attempted.

Preparation.—The gas was prepared by dropping the purest aqueous solution of the acid on phosphorus pentoxide. After passing through tubes containing red phosphorus and phosphorus pentoxide, it was condensed in liquid air, sometimes twice and sometimes once only. In successful experiments the acid was obtained as a pure white solid and a colourless liquid. After an experiment the gas was absorbed over a tube containing soda lime *in vacuo*. Only those experiments in which the impurity was negligible were used for the determination of the index.

Procedure.—The procedure was similar to that adopted for bromine, for, strange to say, the coefficients of expansion and compressibility have not been determined. It was, therefore, necessary to supplement the readings of refractivity by measurements of density. The following values were obtained in six experiments:—

REFRACTIVITY of Hydrobromic Acid. λ = 5461.

Experiment . . .	1,	2,	3,	4,	5,	6.
$(\mu-1)\,10^7\times\frac{D}{d_0 76}$ . .	6167,	6153,	6151,	6141,	6139,	6141.

Mean 6149.

Dispersion.—Assuming this value the following values of the dispersion were obtained from eight experiments :—

TABLE VI.—Dispersion of Hydrobromic Acid.

$\lambda \times 10^8$.	$(\mu-1)\,10^8\,\frac{D}{(d_0 76)}$.		
	Observed.	Calculated.	Difference, 3 – 2.
6707·85	60752	60751	– 1
6438·5	60878	60873	– 5
5790·5	61245	61245	0
5769·5	61256	61260	+ 4
5460·7	61490	61490	0
5209·1	61704	61710	+ 6
5085·8	61824	61830	+ 6
4799·9	62160	62149	–11

Using SELLMEYER'S formula the refractivity can be expressed by the equation

$$(\mu-1)\frac{D}{(d_0 76)} = \frac{5{\cdot}1446 \times 10^{27}}{8668{\cdot}4 \times 10^{27} - n^2}.$$

Calculated values are shown in column 3 and differences in column 4.

Density of Hydrobromic Acid.—As the density of the gas at temperatures higher than 0° C. does not appear to have been previously measured the following values are perhaps worth recording. The degree of accuracy was not carried beyond one part in a thousand, since errors in reading the refractivity were not less than this amount.

The gas was weighed at atmospheric pressure and the temperature of the room, which averaged 19° C., and the values were reduced to 0° C. and 760 by the formula

$$D_0 = D_{tp} \times \frac{T}{273} \times \frac{76}{P}.$$

Three experiments gave, for the weight of a litre, on these assumptions, 3·648, 3·647, and 3·650 gr., the mean of which is 3·6484.

The theoretical weight is 3·61633.

HYDRIODIC ACID.

Previous Determinations.—MASCART found $\mu-1 = {\cdot}000906$ for the D line. The dispersion has not been attempted.

Preparation.—The gas was prepared by slowly dropping pure aqueous solution of the acid on phosphorus pentoxide and proceeding as in the case of hydrobromic acid. The solid obtained on freezing was colourless, but the liquid was usually a pale pink, owing to a trace of dissolved iodine. As the boiling point of HI is far below that of iodine the quantity of iodine subliming, at the boiling point of HI, from this mixture was negligible.

Tests for impurity, similar to those in the case of HBr, were equally satisfactory.

Refractivity, $\lambda = 5461$.—In this case also measurements of refractivity had to be supplemented by those of density as this has not previously been determined carefully.

In three trustworthy experiments the following figures were obtained for the refractivity at the green mercury line :—

$$(\mu-1)\,10^7\,\frac{D}{d_0 76}\ .\ .\ .\ .\quad 9237,\quad 9277,\quad 9260.\qquad \text{Mean } 9258.$$

The mean is taken as the best value.

Dispersion.—From seven experiments the following values were obtained for the dispersion :—

TABLE VII.—Dispersion of Hydriodic Acid.

$\lambda \times 10^8$.	$(\mu-1)\times 10^8\,\frac{D}{(d_0 76)}$.		
	Observed.	Calculated.	Difference, 3 − 2.
6707·5	91087	91089	+2
6438·5	91334	91335	+1
5790·5	92087	92080	−7
5769·5	92106	92109	+3
5460·7	92580	92572	−8
5209·1	93015	93016	+1
5085·8	93257	93259	+2
4799·9	93900	93905	+5

Using SELLMEYER'S equation the refractivity can be expressed by the formula

$$(\mu-1)\,\frac{D}{(d_0 76)} = \frac{5{\cdot}7900\times 10^{27}}{6556{\cdot}4\times 10^{27}-n^2}.$$

The calculated values are shown in column 3 and the differences in column 4.

Density of Hydriodic Acid.—The density of this gas also has not been accurately measured. Calculated in the same way as in the case of hydrobromic acid three experiments gave for the weight of a litre 5·789, 5·791, 5·793, mean = 5·791 gr. The theoretical weight is 5·7151, taking H = 1·008 and I = 126·97, and the weight of a litre of oxygen as 1·4290 gr.

STEAM.

Previous determinations on the refractivity of water vapour are given by DUFET as follows :—

Observer.	Light.	$(\mu - 1)\,10^6$.
FIZEAU	D	254
JAMIN	D	257·9
MASCART	D	257
LORENZ	D	250

No one appears to have attempted the dispersion.

Procedure.—A weighed quantity of distilled water, sealed up in a thin capillary tube, was introduced into the refractometer tube, which was then evacuated and sealed off. On breaking the capillary by a jerk the tube was filled with vapour. After adjusting the tubes between the mirrors of the interferometer the centre of the tube containing the water was first cooled to a known temperature and then the tube was heated till the whole of the water present had evaporated. To the number of the bands read was added a proportionate number for the vapour present at the initial temperature.

In order to eliminate the errors of drift other experiments were made in which the ends of the tube were kept near the maximum temperature required (about 140° C.) and the centre of the tube gradually cooled to the temperature of ice.

Refractivity.—Experiments were made with four charges of water. The results are given below :—

Refractivity of STEAM.

Experiment.	$(\mu - 1)\,10^7 \dfrac{D}{d_0 76}$.	Approximate number of bands read.	Remarks.
(1)	2523	178	Mean of 3 experiments.
(2)	2491	379	" 4 "
(3)	2534	130	" 4 "
(4)	2524	300	" 2 "
Mean of 1, 3, and 4	2527		

It will be seen that the second charge yielded results considerably lower than the other three. The cause of the discrepancy was found to be the unequal distribution of vapour between the main portion of the refractometer tube and the small "appendix" left when the side tube is sealed off. When the temperature of the ends is markedly higher than that of the middle (as it was in this series), the error becomes considerable. Neglecting this experiment we take the mean of the other

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three as the value for the green mercury line. The variations of these experiments indicate that this result is probably correct to 1 part in 500.

Dispersion.—Assuming this value the following table shows the values obtained from seven experiments with the largest charge of water, the number of bands read being about 380 for λ = 5461 :—

TABLE VIII.—Dispersion of Steam.

$\lambda \times 10^8$.	$(\mu - 1)\,10^8 \frac{D}{d_0 76}$.		
	Observed.	Calculated.	Difference, 3 − 2.
6707·85	25028	25027	−1
6438·5	25069	25068	−1
5790·5	25191	25191	0
5769·5	25195	25196	+1
5460·7	25270	25272	+2
5209·1	25345	25345	0
5085·8	25380	25384	+4
4799·9	25495	25490	−5

Using the SELLMEYER equation the refractivity can be expressed by

$$(\mu-1)\frac{D}{d_0 76} = \frac{2{\cdot}62707 \times 10^{27}}{10697 \times 10^{27} - n^2}.$$

The numbers calculated from this expression are shown in the third column and the differences between column 3 and 2 are given in column 4.

OZONE.

Previous Work.—No previous work on the refractivity of ozone is recorded in the usual books of reference. The difficulties are considerable. It is impossible to prepare ozone even approximately pure, and if it were possible it would be inadvisable to do so, since the decomposition of the molecules during the time necessary to measure the refraction and dispersion would introduce fruitful sources of error.

Procedure.—Of the two best methods of preparing the gas, electrolysis of a solution of sulphuric acid has produced the highest percentages of ozone, FISCHER and MASSENEZ* having obtained over 28 per cent. by weight. But the objections to this method seemed to us to outweigh its advantages. It was necessary that the gas used should be absolutely pure oxygen, for the smallest trace of moisture, air or hydrogen would introduce large errors; and in the electrolytic process the gas is produced wet and is mixed with air in the connections. For these reasons the method selected was that of ozonising by means of the silent discharge in a vessel of the type

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* 'Zeit. fur Anorg. Chemie,' vol. 52, p. 229, 1907.

used by BERTHELOT. The average yield was 6 per cent. by volume, but on one or two occasions it reached 10 per cent. We failed to identify the causes which produced these higher yields, and were unable to repeat them, but succeeded in obtaining between 5 and 7 per cent. with fair regularity.

Methods.—As in the case of other gases, the work was divided into two parts (1) the determination of the refractivity for a single wave-length (the green mercury line), and (2) the measurement of the dispersion in the visible spectrum relatively to this value.

For the measurement of the refractivity two methods were employed. In the first of these the quantity of ozone present was estimated by destroying the ozone by heat, and measuring the increase of the gas in volume. In the second, the ozone was estimated chemically by bubbling the mixture of gases through a solution of potassium iodide, and titrating with thiosulphate of soda.

As the results of the enquiry were remarkable the following details may be of interest :—

Dry oxygen, prepared by heating permanganate of potash, and stored in a gas holder over mercury, was led through an ozoniser into the interferometer tube, which was previously evacuated. The interference bands which crossed the field were counted till atmospheric pressure was reached. The pressure was then read by connecting the apparatus with a mercury manometer filled with oxygen and separated from the ozonised gas by a long capillary tube. The temperature of the water bath was observed and the tap which led to the refractometer tube turned off. Having again evacuated the connections the gas in the refractometer tube was allowed to flow slowly into the pump, passing through a spiral of fused silica heated to redness, which effectually destroyed the ozone. From the pump it was transferred to another gas holder over mercury and thence again allowed to flow into the refractometer tube, where its temperature and pressure were again measured. If V_1 is the volume of the ozonised, and V_2 that of the deozonised oxygen, the percentage of ozone is given by $V_2-V_1 = xV_1/200$. In the present case V_1 was about 150 c.c., so that if $x = 8$ the total increase of volume is 6 c.c. In order to determine the value of the refractivity to 1 per cent. it is therefore necessary that the total error in pumping the gas round the cycle should not exceed ·06 c.c. In practice this accuracy was not quite attained. It was necessary to grease stopcocks with a mixture of pure paraffin and vaseline, which will not hold a vacuum indefinitely; while, in order to destroy the ozone, the gas had to be pumped through a spiral 12 inches long of fine capillary bore, which made it difficult to evacuate the last traces from the connections. It was also necessary to know the refractivity of the oxygen very accurately, since an error in this figure is multiplied in the ratio of $100/x$. After a sufficient number of trials had been made to prove that our oxygen was approximately pure, its refractivity was assumed to be that previously determined by us,[*] viz., $\mu-1 = \cdot 0002717$. λ 5461.

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[*] C. and M. CUTHBERTSON, 'Roy. Soc. Proc.,' A, vol. 83, p. 151, 1909.

The following are the details of a typical experiment by this method, in which the refractivity of the deozonised gas was separately determined :—

Part I. Refractivity of the ozonised oxygen—

Bands ($\lambda = 5460 \cdot 7$) 489·9. Length of tube 99·786 cm. Pressure difference 742·2 mm. (corrected). Temperature 16°·25 C.

$$\mu - 1 = \frac{489 \cdot 9 \times 5460 \cdot 7 \times 289 \cdot 25 \times 760 \times 10^{-8}}{99 \cdot 786 \times 273 \times 742 \cdot 2} = \cdot 0002909.$$

Part II. Refractivity of the deozonised oxygen—

Bands 474·2. Pressure difference 764·33 mm. Temperature 14°·7 C.; whence $\mu - 1 = \cdot 00027193$.

Part III. Percentage of ozone—

$$\frac{V_2}{V_1} = \frac{764 \cdot 33 \times 289 \cdot 25}{742 \cdot 2 \times 287 \cdot 7} = 1 \cdot 0354.$$

Thus percentage of ozone = 3·54 × 2 = 7·08.

Part IV. Refractivity of pure ozone—

The refractivity of the mixture is the sum of the refractivities of its components. Let $\mu_{O_3} - 1$ denote that of pure ozone, then

$$7 \cdot 08 \times (\mu_{O_3} - 1) + 92 \cdot 92 \times \cdot 00027193 = 100 \times \cdot 0002909,$$

whence $\mu_{O_3} - 1 = \cdot 000539$.

By this method the following results were obtained :—

TABLE IX.—Refractivity of pure Ozone. (First Method.)

Experiment.	Percentage of ozone by volume.	Refractivity, $(\mu - 1) 10^6 \frac{D}{(d_0 76)}$.	Remarks.
1	9·5	508	
2	7·68	543	
3	7·08	539	
4	6·24	511	
5	6·24	545	
6	6·5	560	
7	3·5	[585]	Not reliable, percentage of ozone too small.
8	8·72	502	
9	7·14	497	
	Mean . . .	525	

Second method. To check these results a second set of experiments was made, in which the quantity of ozone was estimated by chemical tests. This method was found to give more concordant figures.

TABLE X.—Refractivity of pure Ozone. (Second Method.)

Experiment.	Percentage of ozone by volume.	Refractivity, $(\mu - 1) \times 10^6 \dfrac{D}{d_0 76}$.	Remarks.
1	6·09	515	
2	5·47	521	
3	4·86	[495]	Not very trustworthy.
4	6·40	522	
5	6·36	530	
6	7·08	516	
	Mean . . .	516·5	

The results obtained by the two methods are tolerably concordant, and would be even better if the third experiment were omitted.

Their mean is 520·7, but having regard to the smallness of the proportion of ozone present it would be unsafe to rely on this number beyond the second significant figure, and we therefore conclude that the refractive index of pure ozone for the mercury green line is

$$\mu = 1·00052.$$

Comparison with the Refractive Index of Oxygen.—It will be observed that this result is remarkable.

The refractivity of oxygen is ·0002717, and if the third atom of oxygen on joining the molecule had the same refractive effect as in the normal gas we should expect a refractivity $(\mu - 1)\,10^7$ of $\frac{3}{2} \times 2717 = 407·5$.

The experimental value 520 is very largely in excess of this, and indicates the existence of interesting peculiarities in the molecule which may probably be ascribed to the linkage.

Dispersion of Ozone.—Nine experiments were made on the dispersion of mixtures of ozone and oxygen. In each of these the refractive index of the mixture for the green mercury line was separately determined, and the other seven refractivities were calculated with reference to it from the observations as previously described.

The first experiment, being a trial, is omitted, and the refractivity of ozone calculated from the remaining eight as follows:—

TABLE XI.—Dispersion of Mixtures of Ozone and Oxygen.

Experiment.	$(\mu-1)\times 10^8 \frac{D}{d_0 76}$.								Bands read.
	6708	6438	5790	5770	5461	5209	5085	4800	
1	28264	—	—	—	28533	—	28664	—	400
2	28143	28194	28332	28339	28420	28505	28544	28667	491
3	28509	28554	28698	28707	28789	28879	28926	29061	250
4	28500	28555	28683	28702	28789	28879	28927	29054	491
5	28499	28543	28692	28701	28789	28870	28919	29050	499
6	28374	28416	28556	28562	28648	28735	28785	28915	527
7	28365	28410	28553	28559	28648	28737	28782	28910	533
8	28368	28412	28549	28552	28648	28726	28781	28909	538
9	28624	28667	28785	28810	28898	28988	29038	29172	238
Means	28423	28469	28606	28616	28703	28790	28838	28967	
Refractivities of O_2. .	26952	26988	27098	27102	27170	27237	27272	27366	
Refractivities of O_3. .	50764	50968	51514	51624	52000	52375	52621	53290	

Adding together all the values of the refractivities for each wave-length separately, and dividing by the number of experiments, we obtain the refractivities for the average mixture of ozone and oxygen, which are given as "means." Assuming $[\mu_{5461}-1]_{O_3} = {\cdot}000520$ the percentage of ozone in this mixture is found as follows:—

$$520x+(100-x)\,271{\cdot}7 = 100\times 287{\cdot}03, \quad \text{whence} \quad x = 6{\cdot}1764.$$

To find the refractivities for the other seven wave-lengths we have only to use this value and the refractivity for the corresponding wave-length of oxygen which we take from our previous determinations, *vide loc. cit. supra* p. 2. Thus

$$[\mu_\lambda-1]_{O_3}\times 6{\cdot}1764+93{\cdot}8236\times[\mu_\lambda-1]_{O_2} = [\mu_\lambda-1]_{\text{mixture}}.$$

The numbers obtained in this way are shown in the next line.

It is at once noticeable that the dispersive power of ozone is much greater than that of oxygen. And here again, as in the case of chlorine, we find that the curvature of the experimental curve is greater than that calculated. Using $\mu_{6708}-1$ and $\mu_{4800}-1$ we obtain the formula $\mu-1 = \frac{2{\cdot}0414\times 10^{27}}{4221{\cdot}3\times 10^{27}-n^2}$, whence we find $\mu_{5461}-1 = 52082$, whereas the experimental value is 52000.

As in the case of chlorine, the inference is that a second term is required.

AMMONIA.

Previous Determinations.—Previous determinations of the refractivity of ammonia are as follows :—

Observer.	Light.	$(\mu-1)\,10^6$.	Corrected for density.
BIOT and ARAGO . . .	White	381	
DULONG	„	383	
MASCART	D	377	376 ?
LORENZ	Li	371	
„	D	373	373
G. W. WALKER . . .	„	379·3 ± ·5	374·3

It would occupy too much space to analyse the causes of these discrepancies, which are chiefly due to differences in the standard conditions assumed and in the coefficients of thermal expansion and compressibility adopted. But the figures in the last column give approximately the figures corrected for the theoretical density.

Preparation.—Our gas was prepared by warming a mixture of ammonium chloride and calcium oxide in a flask. After passing over red hot lime and cold dry lime it was condensed at −80° C. and allowed to boil off, the middle fraction being collected. Three samples were used.

Calculation of Results.—In reducing the results the figures given below were used, following GUYE[*] :—

Coefficient of thermal expansion $(1+\cdot003914t)$.

Coefficient of compressibility

$$1-\frac{p_1v_1}{p_0v_0} = A\,(p_1-p_0), \qquad A = \cdot0002\,(1-\cdot000003t).$$

Weight of a litre of ammonia at 0° C. and 760 mm., ·7708 gr. Theoretic density, ·7605 gr.

Thus the equation for reduction is

$$(\mu-1)\,\frac{D}{(d_0 76)} = \frac{N\lambda}{L}\,\frac{7605}{7708}\times 76\Big/\frac{p_1\,[1-A\,(76-p_1)]}{1+\cdot003914t_1}-\frac{p_2\,[1-A\,(76-p_2)]}{1+\cdot003914t_2},$$

where N is the number of bands observed, λ the wave-length, L the length of the tube, and p_1p_2, t_1t_2 the initial and final pressures and temperatures.

Refraction.—The determinations for λ 5461 were, as usual, made by pairs of experiments, with pressure rising and falling.

The mean of nine such experiments, whose extremes were 1·0003782 and 1·0003790,

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[*] 'Mém. Soc. de Phys. et d'Hist. Nat. de Genève,' vol. 35, 1908.

was 1·0003786. Seven of these were at room temperature and two at 0° C. We adopt ·0003786 as the refractivity for the green mercury line.

Dispersion.—Five experiments were made to determine the dispersion.

The following table gives the mean results and compares the observed values with those calculated from the formula

$$\mu-1 \frac{\mathrm{D}}{d_0 76} = \frac{2{\cdot}9658 \times 10^{27}}{8135{\cdot}3 \times 10^{27} - n^2},$$

which was, as usual, calculated from the observations by the method of least squares :—

TABLE XII.—Dispersion of Ammonia.

$\lambda \times 10^8$.	$(\mu-1)\,10^8 \frac{\mathrm{D}}{(d_0 76)}$.		
	Observed.	Calculated.	Difference.
6707·85	37376	37374	−2
6438·5	37455	37456	+1
5790·5	37701	37700	−1
5769·5	37707	37710	+3
5460·7	37860	37861	+1
5209·1	38002	38006	+4
5085·8	38083	38085	+2
4799·9	38300	38295	−5

NITRIC OXIDE. (NO.)

Previous Work.—DUFET gives the following :—

Light.	$(\mu-1)\,10^6$.	Observer.
White	302	DULONG.
D	297·1	MASCART.

Mr. E. P. METCALFE, in collaboration with one of us,* obtained 293·9 for λ = 5893. The gas used by MASCART had 10 per cent. of impurity.

Preparation.—Following the third method described by GUYE† we prepared the gas by the action of of dilute sulphuric acid (10 per cent.) on dilute nitrite of soda (6 per cent.) in a vacuum. After bubbling through concentrated sulphuric acid and passing over P_2O_5 it was condensed in liquid air and fractionally distilled. The gas employed, tested with ferrous sulphate, showed less than 1 part in a 1000 of impurity,

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* C. CUTHBERTSON and E. P. METCALFE, 'Roy. Soc. Proc.,' A, vol. 80, p. 406, 1908.

† GUYE, 'Mém. Soc. de Phys. et d'Hist. Nat. de Genève,' vol. 35, p. 547, 1908.

probably nitrogen. As the refractivity of nitrogen is almost identical with that of nitric oxide the results were not modified by the impurity. The observations were reduced by the ordinary formula $\mu-1 = (\nu-1)\,\frac{T}{273} \times \frac{76}{P}$.

Refraction.—Six careful double experiments (*i.e.*, pressure rising and falling) gave

Experiment	1,	2,	3,	4,	5,	6.	
$(\mu-1)\,10^7\,\frac{D}{(d_0 76)}$ . . .	2959,	2957,	2952,	2955,	2951,	2956.	Mean 2955.

We adopt this mean ·0002955 as the value for the green mercury line.

Calculating the value for the D line from this value and the dispersion formula obtained below we find ·0002944, which agrees well with 2939 found in 1908.

Dispersion.—From five observations the following values for the dispersion were obtained :—

TABLE XIII.—Dispersion of Nitric Oxide.

$\lambda \times 10^8$.	$(\mu-1)\,10^8\,\frac{D}{d_0 76}$.		
	Observed.	Calculated.	Difference.
6707·85	29306	29302	−4
6438·5	29344	29344	0
5790·5	29468	29469	+1
5769·5	29474	29474	0
5460·7	29550	29553	+3
5209·1	29622	29628	+6
5085·8	29666	29668	+2
4799·9	29776	29776	0

Using SELLMEYER's formula the results are expressed by

$$(\mu-1)\,\frac{D}{(d_0 76)} = \frac{3{\cdot}5210 \times 10^{27}}{12216 \times 10^{27} - n^2}.$$

NITROUS OXIDE. (N_2O.)

Previous Work.—DUFET gives

Light.	μ.	Observer.
White	1·000507	DULONG.
Red	1·000507	JAMIN.
6439·2	1·0005132	MASCART.
—	1·0005152	,,
5378·9	1·0005192	,,
5086·1	1·0005207	,,
4800·2	1·0005230	,,

MASCART'S gas was prepared from ammonium nitrate and contained 10 per cent. of impurity.

The gas we used was obtained from two sources: (1) The commercial gas, obtained in cylinders, condensed and fractionated at the temperature of liquid air, and (2) gas prepared by the action of ammonium nitrite on hydroxylamine hydrosulphate. It was bubbled through strong potash and dried with sulphuric acid and phosphorus pentoxide.

Refractive Index.—Three sets of experiments on different samples gave

Series.	$(\mu-1)\,10^7\,\frac{D}{(d_0 76)}$.	Source.
1	5092	Commercial.
	5102	
2	5097	,,
	5098	
	5099	
3	5087	From hydroxylamine.
	5091	
Mean . . .	5096	

In reducing these experiments the coefficient of thermal expansion used was ·00371.

The purity of the gas was tested by absorption in an excess of water boiled *in vacuo.* The bubble of gas left unabsorbed was not so great as 1/2000 of the whole; and even this was probably due to the error of the test experiment, which is not very easy. But as traces of air were probably present we think 5100 a more trustworthy value than the exact experimental mean, and probably correct to 1/500 at least.

Dispersion.—From five experiments the following values were obtained for the dispersion :—

TABLE XIV.

$\lambda \times 10^8$.	$(\mu-1)\,10^8\,\frac{D}{(d_0 76)}$.		
	Observed.	Calculated.	Difference.
6707·85	50544	50540	−4
6438·5	50616	50616	0
5790·5	50848	50848	0
5769·5	50857	50857	0
5460·7	51000	51003	+3
5209·1	51145	51142	−3
5085·8	51208	51215	+7
4799·9	51415	51420	+5

The refractivity can be expressed by the formula

$$(\mu-1)\frac{\mathrm{D}}{(d_0 76)} = \frac{5\cdot 6685\times 10^{27}}{11416\times 10^{27}-n^2}.$$

The calculated values are shown in column 3 and the differences in column 4.

Errors of Experiment.

Refraction.—In the determination of the refractivities for the green mercury line the principal source of error is the impurity of the gas, and, in the case of vapours which absorb light, such as the halogens and sulphur, the limitation of the number of bands which can be read before the light fails.

It will be seen that experiments of a series generally agreed to 1 part in 500, and the mean is probably within 1 in a 1000 of the truth. In iodine and ozone, however, the errors may amount to 1 or 2 per cent.

Dispersion.—It will be observed that the values of the refractivities for the other seven wave-lengths are relative to that found for the green mercury line.

The degree of accuracy attainable depends on the number of bands read and the dispersive power of the gas. As an example take nitric oxide.

Here $[\mu-1]_{\lambda=6708} = \cdot 00029306$, $[\mu-1]_{\lambda=4800} = \cdot 00029776$.

The dispersive power is $\frac{29776-29306}{29776} = \frac{470}{29776}$; and if 400 green bands are counted, the number which represents the effect of dispersion is $\frac{188000}{29776} = 6\cdot 3$ bands. We consider that 1/15 of a band can be read; so that the value of the dispersive power should be correct to 1 part in 95. It may be assumed that by determining the constants from eight independent values of the refractivity instead of two the accuracy is at least doubled, and the error should not exceed 1/200 of the effect itself.

This claim is supported by the experimental results. Thus, in the six experiments from which the dispersion of HCl was determined, the values of $(\mu_{6708}-\mu_{4800})\times 10^8$ were 816, 815, 813, 818, 805.

In eight experiments on HBr they were 1370, 1388, 1393, 1356, 1372, 1376, 1368, 1363.

Calculation of the Constants.

The calculation of the constants N and n_0^2 of the formula $\mu-1 = \mathrm{N}/(n_0^2-n^2)$ by the method of least squares is very laborious if carried out in the ordinary manner. The following modification was, therefore, adopted. Using subscripts to denote the eight refractive indices and their frequencies we have eight equations of the form

$$\frac{1}{\mu_1-1} = \frac{n_0^2-n_1^2}{\mathrm{N}}.$$

Subtracting the $(n+4)^{\text{th}}$ from the n^{th} equation, we obtain four equations similar to

$$\frac{1}{\mu_5-1}-\frac{1}{\mu_1-1}=\frac{1}{\mathrm{N}}\{n_5^{\,2}-n_1^{\,2}\}.$$

Let $\dfrac{1}{\mu_5-1}-\dfrac{1}{\mu_1-1}$ be expressed by x, and $(n_5^{\,2}-n_1^{\,2})$ by y, and similarly for the other three equations. Then it can be shown that, applying the method of least squares,

$$\mathrm{N}=\Sigma\,(x\,.\,y)/\Sigma\,(x^2),\quad\text{and hence}\quad n_0^{\,2}=\tfrac{1}{8}\mathrm{N}\left\{\Sigma\left(\frac{1}{\mu-1}\right)\right\}+\Sigma\,(n^2).$$

We have much pleasure in recording our deep obligations to many friends. To Prof. TROUTON and Prof. A. W. PORTER we owe most grateful thanks for their unwearied patience in assisting, guiding, and encouraging us. To Prof. N. WILSMORE and Dr. WHYTLAW-GRAY we are indebted for instruction and invaluable help in the whole of the chemical side of the work. To the Royal Society we owe our grateful acknowledgment for the assistance of pecuniary grants.