On the Refractive Indices of the Elements

Clive Cuthbertson

Phil. Trans. R. Soc. Lond. A 1905 **204**, 323-349
doi: 10.1098/rsta.1905.0008

VIII. *On the Refractive Indices of the Elements.*

By CLIVE CUTHBERTSON.

Communicated by Professor F. T. TROUTON, *F.R.S.*

Received October 18,—Read November 24, 1904.

THE relation between the constitution of the molecules of compounds and their power to retard the velocity of light is a subject which has attracted many observers, and has led to results which are interesting, both from their general regularity and occasional discrepancy. It is singular, therefore, that so few attempts have been made to investigate that portion of the subject which should, theoretically, have occupied a prior place, the study of the refractive indices of the elements in the gaseous state and their relation to one another.

No doubt this defect in our information is due to the difficulty of obtaining all but a very few elements in such a state that their index of refraction can be measured directly. Till recently, the only elements in which this had been done were H, N, O, Cl, Br, I, Hg, S, P, and As; and the numbers obtained in these instances did not seem to bear any relation to each other, or to any known constant. Thus, the refractivities* of Cl, Br, and I increase with the increase in their atomic weights, though not proportionately. But O, with an atomic weight sixteen times that of H, only retards light twice as much, while the index of N is actually greater than that of O. Discouraged by these anomalous results, investigators have generally contented themselves with calculating values for the refractivities of the elements from the effects they produce in compounds, and have aimed at obtaining an empirical constant for each element which would satisfy an additive law in compounds. The numbers so obtained are found to vary with the constitutional formula of the compound in question, and the variations are sufficiently regular to afford assistance in analysing the constitution of complex molecules; but even the best results sometimes fail to fit in with the facts in a way which proves that our empirical formulæ are still far from the truth.

In 1901, however, the *data* at disposal received a notable enlargement by the discovery of argon and the other members of the family of inert gases. These

---

* In the following paper the word "refractivity" is equivalent to the expression $(\mu - 1) 10^6$.

elements, He, Ne, A, Kr, and X, are of peculiar importance in the study of optical constants. They are all elements. They are all gases at the ordinary temperature. And they are all members of the same chemical family and of zero valency. In all, too, the molecule is monatomic, so that whatever complication may be caused by the expenditure of radiant energy on internal work in the molecule may be presumed to be absent. Any relation, therefore, which exists between the refractivities of the elements may be expected to show itself more clearly in this chemical group than in any other.

The refractive indices of all five gases have been measured by Sir WILLIAM RAMSAY and Dr. TRAVERS, and are given in their paper published in the 'Philosophical Transactions.'*

In a letter, published in 'Nature' of October 16th, 1902, I drew attention to the fact that these figures bear to each other a curiously simple relation. Within narrow limits of divergence, easily accounted for by the difficulty experienced in purifying the gases, and the smallness of the quantities with which the experiments were made, the refractivities are in the proportion of 1, 2, 8, 12, and 20; or, more simply, of $\frac{1}{4}$, $\frac{1}{2}$, 2, 3, and 5, as shown in the following table:—

TABLE I.

Element.	Refractivity (air = 1).	Refractive index (air = 1·000293).	Refractivity $(\mu - 1)\,10^6$.	Ratios.	Refractivities calculated.	Divergence per cent., columns 4 and 6.
Helium . .	0·1238	1·0000363	36·3	$\frac{1}{4}$	35·5	+ 2·3
Neon . . .	0·2345	1·0000687	68·7	$\frac{1}{2}$	71	− 3·2
Argon . .	0·968	1·000284	284	2	284	—
Krypton . .	1·450	1·000425	425	3	426	− 0·2
Xenon . .	2·352	1·000689	689	5	710	− 3·0

In the calculation given in column 6 the value for argon is taken as the standard, since it is the most easily purified. The discrepancies are not large, and it is remarkable that in three cases out of four they take the direction which admixture with a neighbouring element would cause them to do. Thus, it is difficult to separate He and Ne, and we find that the refractivity of the former is too high and of the latter too low. Similarly, the number obtained for X is too low, as would be the case if the specimen contained any Kr.

It is highly improbable that the ratios of these five numbers should approach so nearly to integers by mere accident; and the question naturally arises whether any similar relation can be traced between the refractivities of the members of the other chemical groups.

---

* 'Phil. Trans.,' A, vol. 197, p. 81, 1901.

We are, fortunately, in possession of the figures for another similar family, the halogens, whose indices have been determined in the gaseous state by several independent observers. The following table exhibits these results, and shows that, in this series also, the refractivities are in the relation of 2, 3, and 5, within very narrow limits of accuracy.

Table II.

Element.	Refractive index.	Refractivity $(\mu - 1) 10^6$.	Ratios.	Refractivities calculated.*	Divergence per cent., columns 3 and 5.	Observer.
Chlorine . .	1·000768	768	2	768	—	Mascart
Bromine . .	1·001125	1125	3	1152	−2·3	"
Iodine . .	1·00192 violet†	1920	5	1920	—	Hurion
	1·00205 red	2050	—	—	+6·4	"

In estimating the significance of these figures, it must be remembered that the atomic weights of Cl, Br, and I are not far from those of A, Kr, and X; so that, if the refractivity should turn out to be a function of the atomic weight alone, the weight of the evidence against the possibility of chance is not materially increased by the inclusion of this group. But if, as there are reasons for believing, the refractivity is, in reality, a complicated function of atomic weight, valency, and other properties of matter, great importance must be attached to the corroboration afforded by this second series of coincidences.

When the inquiry is extended to the other elements whose refractive indices have been measured, we find that the evidence, resting as it does on the results of a single difficult research, undertaken more than forty years ago, is not of a conclusive character, and that the figures are perplexing. In 1861 the refractive indices of Hg, P, S, and As were determined, in the state of vapour, by M. Le Roux,‡ who obtained the values shown in the following table.

The last four lines are the figures of Dulong for the permanent gases, with which M. Le Roux compared his results. But in making the comparison it must be remembered that the "absolute indices" shown in column 2 are calculated for the state of aggregation of molecule which is found by experiment. Hence, to compare the index of a vapour with a gas, the fractional part of the indices must be divided by the number of atoms in their molecules.§

---

* Chlorine is taken as the standard. M. Mascart's values are for sodium light. M. Dulong obtained the same figure for chlorine for white light.

† Iodine shows anomalous dispersion. The lower value for the violet rays is that which fits in best. The higher value differs from the lower by 6·4 per cent. But the index of iodine should be re-determined. Hurion's readings varied 5 per cent. in the red and 7 per cent. in the violet.

‡ Le Roux, 'Annales de Chimie,' vol. 61, p. 385, 1861.

§ A similar correction is required in the case of the figures for the inert gases given by Ramsay and Travers when compared with gases whose molecules are diatomic.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE III.

Substances.	Indices absolus.	$(m^2-1)\times 1000$.	Densité (Air = 1).	$\frac{(m^2-1)\times 1000}{\text{D}}$ (Pouvoir réfringent).	Equivalent, H = 1.	Produit de pouvoir réfringent par équivalent.
Soufre . . .	1·001629	3·258	6·617	0·492	16	7·87
Phosphore . .	1·001364	2·728	4·355	0·626	31	19·41
Arsenic . . .	1·001114	2·228	10·39	0·214	75	16·08
Mercure. . .	1·000556	1·112	6·976	0·159	100	15·93
H.	1·000138	0·277	0·0692	4·003	1	4·003
O.	1·000278	0·544	1·1056	0·4924	8	3·939
N.	1·000300	0·601	0·9713	0·6187	14	8·661
Cl.	1·000772	1·544	2·44	0·6328	35·5	22·464

The number given for the refractivity of Hg (556) is exactly four times the accepted modern value for H_2 (139), while that for S_6 (1629) coincides almost equally closely with a multiple of the accepted modern value of O_2 (270). But the figures found for P and As bear no such simple relation to each other, or to the refractive index of N, the first member of the same chemical group. Unless, therefore, the results of M. LE ROUX were inaccurate, it appeared that no simple generalisation could be made which would embrace all the elements whose indices were known. But the coincidences exhibited by the halogens and the inert gases were so striking as to induce me to attempt to repeat the work of the French physicist, and to verify his conclusions. In this desire I was encouraged by the fact that M. LE ROUX himself speaks of the accuracy of his results with diffidence, owing to the great difficulties involved in the experimental method he employed.

The earliest researches on the indices of the permanent gases were made with a hollow prism, but this was afterwards abandoned for the more accurate method of interference bands. But, having to deal with substances whose vapour density is inconsiderable except at high temperatures, for which the interference method seemed unsuitable, M. LE ROUX reverted to the older plan. He constructed a hollow prism-shaped chamber of iron, 18 centims. in length and 7 centims. in height, having two glass faces inclined at an angle of 125°. The glass was luted to the iron with a mixture of nitrate of potash and carbonate of lime. In this prism he placed a fragment of the element whose refractive index was to be measured, and the whole apparatus was heated in a furnace to a temperature which was approximately equal to its boiling-point. When the heating had continued sufficiently long to satisfy him that the last traces of air had been displaced from the interior of the prism, he measured the deviation produced by the presence of the vapour by observing a distant point of light through a telescope. From this observation he was enabled to calculate the ratio of the refractive index of the substance to that of air at the same temperature and pressure, and thence to deduce the index under standard conditions.

It is obvious that this method is open to many objections, the gravity of which was fully recognised by the experimenter. Indeed, in the case of arsenic, no great accuracy was even claimed. It seemed probable, therefore, that, by using a more accurate method, better results might be obtained. The plan adopted by nearly all students of the refractivity of gases since LE ROUX has been that of interference, and the instrument employed is JAMIN'S refractometer. M. MASCART, however, made use of TALBOT'S bands in his researches on the refractivities of vapours, and preliminary experiments were accordingly made to determine the comparative advantages of the two plans. In the end JAMIN'S method was selected.

The principle of the instrument, and its adaptation for measuring the indices of gases, are too well known to need description. In the case of vapours the procedure which seemed to promise best was to introduce into one of the two parallel tubes some of the element whose index was sought, and to evacuate and seal off both tubes. When this system is placed in position in the refractometer, and the tubes are heated by means of an electric furnace, the path of that ray which passes through the empty tube is unaltered within the tube. But the ray which traverses the tube containing the substance is gradually retarded by the increasing density of the vapour produced by heating. If the number of bands which pass over the field and the density of vapour in the tubes are known, the refractive index can be calculated.

In adapting JAMIN'S apparatus to the measurement of the indices of substances which are not gaseous, except at high temperatures, several difficulties presented themselves. The first, and most serious, was to find some way of effecting so perfect a junction between the tube and the glass plate with which its end was closed that it would hold a vacuum for several hours at a temperature of, at least, 300° C. M. MASCART, in his researches on the indices of vapours, did not use any temperature higher than 50° C., and the ends of his tubes were made air-tight by pressing the plates of glass against a ring of caoutchouc. For higher temperatures this plan is useless, and, consequently, new means had to be sought. Various devices were tried, and, after about two months' work, it was found that the desired result could be obtained by stopping the ends of the tube with discs of plate glass, ground conical, and covering the junction with sealing-wax, or, better still, with shellac. Tubes fitted with these ends have acted well; but it is necessary that the tube itself should be of moderately hard glass, otherwise the unequal expansion of the tube and plate glass end causes the former to crack with unfailing regularity. It was calculated that, at any rate for Hg, S and P, a temperature of not more than 300° C. would produce such a vapour density as would suffice; and, to obtain this, a primitive form of electric furnace was constructed which could raise the temperature of the enclosed space to 270° C. in about an hour, and could attain 300° C. with difficulty in two hours. The tubes, which were about 37 centims. long, were placed in the axis of the furnace, which projected about 10 centims. beyond each end.

The next difficulty which threatened to be serious was that due to the shimmering produced by currents of unequally heated air. The distance between the two mirrors of the refractometer cannot be indefinitely increased; and the gradient of temperature between the furnace and the air outside must necessarily be steep. In fact, the whole fall of temperature occurred in a distance of about six inches. It appeared probable that the mirage effects would make it impossible to read the bands. This danger was, however, completely met by a device previously used by M. LE ROUX. In each end of the furnace three diaphragms of ordinary plate glass were inserted, separated by distances of about an inch, and the internal cylinder of the furnace was prolonged by a paper tube four inches long, which deflected the air currents. By this means all flicker was avoided, and, during an experiment, the bands appeared to pass perfectly steadily, even when the temperature was at its highest point. So far as this cause of error was concerned, there was no difficulty in reading the bands to $\frac{1}{10}$ of their breadth.

Having determined the form of the apparatus, the next point for consideration was the means to be adopted for estimating the amount of vapour present in the tube.

Mercury was the first substance upon which experiments were made, and, since its vapour pressure at various temperatures has been determined with considerable accuracy by RAMSAY and YOUNG* and others, the plan originally tried was to measure, by means of thermometers, the temperature of the coldest part of the tube, and to assume that the density of vapour throughout the tube was that which corresponded to this temperature. Numerous experiments were made with this method, but the results were not satisfactory. The errors due to the calculation of the appropriate stem correction, and to the difference of temperature between the outside and the inside of the tube, were sufficient to cause a variation of 25 per cent. in the results, and the method was consequently abandoned.

The alternative plan, next adopted, was to weigh a quantity of the substance sufficient to cause a convenient number of bands to cross the field, to introduce this into the tube, and then to heat it in a vacuum until the whole amount had passed into the form of vapour. This method proved far superior to the other, and was perfectly successful. All measurements of temperature and pressure are avoided, and the density of the vapour is calculated from the weight of the substance vapourised and the volume of the tube, both of which can be measured very precisely.

Before stating the results obtained for different substances, it will be convenient to describe the dimensions of the apparatus and the details of the procedure adopted in an experiment.

The tubes employed in the refractometer were of moderately hard glass, 36 to

---

* RAMSAY and YOUNG, 'Trans. of Chem. Soc.,' vol. 49, p. 37, 1886.

37 centims. in length, 1 centim. in diameter, and about ·15 centim. in thickness of wall. Into their ends were fitted discs of ordinary plate glass, 9·2 millims. thick, ground slightly conical. About $\frac{3}{5}$ of the thickness of the plate was in contact with the wall of the tube, the remaining $\frac{2}{5}$ projecting beyond its end. At the middle point of the tube, and at right angles to it, a side tube of smaller diameter was sealed, and, close to the junction, the side tube was contracted, so that it could be sealed off easily after being exhausted, leaving a very short "appendix" which would not project beyond the inner circumference of the electric furnace. After thoroughly cleaning the tubes a pair of discs was fitted in (one in each tube), and one of the two was rotated till interference bands could be seen in the field of the telescope. The other pair was then similarly adjusted.*

The tubes were then heated to about 120° C., and a thin layer of shellac was laid round the junction of tube and disc. The tubes were next exhausted and re-heated, and the shellac allowed to cool and harden under external pressure. Prepared in this way, the junctions stood the effect of both temperature and pressure perfectly for some time. After about a dozen experiments, the shellac would become slightly porous, but this was easily remedied by a fresh coating. At the first heating, shellac softens at about 120° C., but, after prolonged heating, it appears to lose its more volatile constituents, and sets into a hard, almost black, mass, which adheres to glass, and does not soften or char below 300° C.

A weighed quantity of the substance whose refractive index was to be measured was then introduced into one of the tubes by the side tube, with the precautions demanded by its chemical nature which are given below. The tube was evacuated with a Fleuss pump, and the side tube sealed off as close as possible to the main tube.

The other tube was not sealed off, but was left in connection with a pump and manometer throughout the experiment, so that a leak, if any occurred, could be detected at once.

The two tubes were laid side by side, enveloped in a jacket of iron plate, which served to equalise the temperature, and to hold them together. They were then placed on two crescents of asbestos which fitted the inside of the furnace, and maintained them symmetrically in the centre of the cylinder, equidistant from its sides. The two halves, in which the electric furnace was made, were now drawn together over the tubes, and the junction carefully packed with asbestos, a thermometer, for rough observations of temperature, being inserted with its bulb in contact with the glass of the tubes at their middle point, which was usually the coolest portion of the system. Finally, the whole was adjusted between the mirrors of the refractometer till interference bands could be seen in the field of the telescope. A pointer was hung on the mirror furthest from the eye to mark the zero of observation.

---

* This adjustment is necessary owing to the fact that it is very difficult to grind a stopper so truly that the axis of the cone which it forms is accurately at right angles to the plane of the plate.

The tube which remained in connection with the pump was then exhausted, and the height of the mercury in the manometer noted. The observer, having taken his seat at the telescope and noted the position of the bands, turned on the electric current. The tubes slowly warmed, and in about an hour had reached a temperature of 270° C. As the substance grew hot it began to volatilize, and the bands which slowly crossed the field were counted. When that temperature was reached at which all the substance present had passed into vapour, the bands ceased to move with remarkable abruptness. When this had occurred the temperature was allowed to rise about 10° C. further, to make sure that no more of the substance was still lurking unevaporated in any cool corner of the tube. The manometer was again noted, and was seldom found to have varied as much as a millimetre, in spite of several rubber connections. The supply of heat was then cut off, and the bands again counted, as they retreated, owing to the condensation of the vapour. Lastly the manometer was again read. Thus, in each experiment two readings were obtained.* After making the necessary corrections these two readings coincided very closely, and thus furnished a valuable proof of the absence of leaks.

When the tubes had cooled to such a point that no further movement of the bands could be detected, the tube containing the substance was taken out of the furnace and examined. In a good experiment the whole of the element volatilized was found condensed in the portions of the tube which had successively become coolest as the temperature fell, and unless the deposit looked perfectly clean and unoxidised the experiment was discarded. This tube was then opened at the extremity of the appendix, and its volume measured by weighing it empty and full of distilled water. Its length was also measured.

From these data the calculation of the refractive index is simple. What we wish to compare is the retardation of light caused by the presence of equal numbers of the atoms of different elements. In the case of the permanent gases the indices are calculated for standard temperature and pressure, and it is assumed that the numbers of molecules are then equal. If the state of aggregation of the molecule is also known, the materials for comparison are complete. In the case of vapours we measure the retardation of light produced by a known density of vapour, and calculate what the retardation would be if the number of atoms per unit volume were the same as they are in the case of the permanent gases at normal temperature and pressure. This is the case when the density of the vapour bears to that of a gas the ratio of their respective atomic weights. Hence, we have only to multiply the refractivity observed in an experiment by the ratio of the standard to the observed density in order to obtain the index of refraction. In the present case the density of the vapour employed is calculated from the weight of the element evaporated and the volume of the tube, and the standard density chosen is that of H_2 (·0000899)

---

* At least in the later experiments. In the earlier the upward run was lost owing to moisture condensing on the diaphragms. This was afterwards obviated by a preliminary heating of the apparatus.

multiplied by the ratio of the atomic weights of the element and H (taken as 1·007). Hence, the results are comparable to the well-known figures for the permanent gases, whose molecules are diatomic.

If N be the number of bands observed to pass the pointer as the whole of the substance evaporates, λ the wave length of light employed, X the length of the tube, m the refractive index observed and μ the refractive index at the standard density, we have $N\lambda = (m-1)X$ and

$$\frac{\mu-1}{m-1} = \frac{\text{standard density}}{\text{observed density}}$$

$$= \frac{\cdot0000899 \times \text{atomic weight of element}}{\text{atomic weight of hydrogen}} \times \frac{\text{volume of tube}}{\text{weight volatilized}}.$$

Hence

$$\mu-1 = \frac{N\lambda}{X} \frac{\cdot0000899 \times \text{atomic weight of element} \times \text{volume of tube}}{\text{atomic weight of hydrogen} \times \text{weight volatilized}}.$$

The legitimacy of this method of comparison rests on the assumptions that the refractivity is proportional to the density, and is independent of the temperature if the density remains constant. The former is the conclusion accepted by M. MASCART, and, I believe, all other observers. With regard to the latter, opinion is divided, but, as a first approximation, and to the degree of accuracy sought in these observations, it is almost certainly true.* So far as my experience goes it confirms this belief. When the substance had completely evaporated, no subsequent rise of temperature, even by as much as 20° C., had any effect on the position of the bands.

Sources of Error.

The principal source of error detected in the refractometer method is that which may be called the starting effect. It frequently happened that, when the heating began, the bands shifted by an amount which generally varied between ½ and 1 band. In a few minutes the displacement seemed to reach a limit and then, after a pause, short or long in proportion to the volatility of the substance, the true procession of bands began.† Sometimes the shift took place in the direction in which the bands were about to move, sometimes in the opposite direction. Similarly, when the temperature had reached its highest point and the heat was cut off, the bands sometimes shifted slightly before the main fall began.

This effect is probably due to unequal heating of the tubes, or of the columns of air outside the tubes through which the rays respectively passed. The error could be to

---

[*] See G. W. WALKER, 'Phil. Trans.,' A, vol. 201, p. 435, 1903, "On the Dependence of the Refractive Index of Gases on Temperature."

[†] By a series of blank experiments it was shown that the effect did not increase as the temperature rose.

a large extent allowed for by observing the position of the bands when the preliminary shift ceased and counting the true procession of bands from this starting point.

It is probably owing to this cause that the experiments in which the number of bands was small yielded the most discrepant results.

Leaks.—In the case of the tube which remained in connection with the manometer a leak could not remain undetected. In the tube containing the substance a leak would produce a discrepancy between the number of bands observed in the upward and downward grades of temperature, and the concordance of the two observations is the test by which such a source of error could be detected.

A considerable leak would, in the cases of mercury and phosphorus, produce solid compounds visible to the eye. No experiment was accepted as trustworthy in which these tests did not give negative results.

Reading the Bands.—With the aid of a pointer in the field of view the position of the bands could generally be estimated to $\frac{1}{5}$ of their breadth, and sometimes I believed my reading to be accurate to $\frac{1}{10}$ of a band.

Weighing.—The substances used were weighed on a good long-armed balance, accurate to ·01 of a milligramme, or $\frac{1}{270}$ part of the smallest quantity ever employed (usually much less). The weight of mercury was obtained from the difference of the weights of a capillary tube empty and full of mercury. The sulphur and phosphorus were weighed by BORDA's method.

Corrections.

Inequality in the Length of the Tubes.—When an experiment was performed with a tube which had been broken and mended, the two tubes sometimes differed in length by as much as a millimetre, and a correction had then to be made for the variation of the retardation of light in passing through a layer of air equal to this difference, as its density varied with the temperature.

If the difference of length was 1 millim. and the limits of temperature 15° C. and 270° C., the correction only amounted to $\frac{1}{4}$ of a band, so that the error due to an inaccurate estimate of these limits is inappreciable.

Change of Dimensions with Change of Temperature.—The refractivity is directly proportional to the volume of the tube when the temperature is highest, and inversely to its length; and since both these measurements are made at the temperature of the air, the observed refractivity has to be multiplied by $1+2a(t_1-t_2)$, where a is the linear coefficient of expansion of glass and t_1 and t_2 the limits of temperature.

Unfortunately, the coefficient of expansion was not measured for each tube at the time, and, as the numerous tubes all ultimately broke and the upper limit of temperature was not exactly known, the correction cannot be made accurately. But, as its gross amount does not exceed $\frac{1}{2}$ per cent., we shall not err by 1 part in 1000 by assuming a mean value of ·000008 for a and a mean range of temperature of 250° C. − 15° C. = 235° C. for all the experiments. Hence

$$1+2a(t_1-t_2) = 1{\cdot}0038,$$

and this correction is made on the mean value obtained for the refractivities of Hg, P and S.

Degree of Accuracy.

The degree of accuracy aimed at was no greater than one per cent. The inquiry was undertaken with the object of discovering whether any simple numerical relation subsisted between the refractivities of members of the various chemical families, similar to that observed in the cases of the inert gases and the halogens. If such a relation did subsist, it was not likely that experiments made with light of a wave-length arbitrarily selected* would exhibit a higher degree of concordance, since the dispersion, within the limits of the visible spectrum, is generally at least as great as 1 per cent. of the refraction. A higher degree of accuracy could only have been attained by the sacrifice of more time than was advisable, having regard to the time spent on each experiment, which generally took about a week to prepare.

I much regret that the number of experiments, especially in the case of sulphur, was not larger; but it seemed at the time that more would be gained than lost by attacking a new substance, as soon as it became clear that concordant results were being attained.

With these general observations I pass to a record of the results obtained.

Mercury. (Atomic Weight = 200·3.)

Mercury was the first substance with which experiments were made. No special precautions were taken to obtain the substance absolutely pure, since the percentage of impurity in good, clean mercury must be very small.

As has been stated above, the plan first adopted was to put excess of mercury in the refractometer tube, and to calculate the density of the vapour present from an observation of the temperature of the tube at its coldest part, by means of the table connecting the temperature and vapour-pressure of mercury given by RAMSAY and YOUNG. Though the method ultimately proved a bad one, owing to the difficulty of measuring the temperature accurately, I give below the details of all the experiments performed by this method, since they are sufficiently concordant to corroborate roughly the results subsequently obtained by the balance method, and to show that the true value of the index of mercury is of a different order from that obtained by LE ROUX.

---

* The figures are for sodium light throughout, and the wave-length is taken at 5893.

TABLE IV.—Refractive Index of Mercury. Preliminary Experiments.

Date.	Length of tube.	Number of bands observed.	Temperature of coolest part of tube.	Vapour-pressure at this temperature.	Refractive index for Hg_2.
	centims.		° C.	millims.	
February 14, 1903	35·2	$26\frac{1}{2}$	240	56·9	1·00223
„ 20, 1903	35·2	$38\frac{1}{2}$	$256\frac{1}{2}$	88·5	1·00215
March 9, 1903 .	35·4	$29\frac{1}{2}$	$239\frac{1}{2}$	56	1·00250
„ 12, 1903 .	35·05	$19\frac{3}{4}$	$231\frac{1}{2}$	44·5	1·00208
„ 13, 1903 .	35·05	37·4	254	82·6	1·00224
„ 14, 1903 .	35·05	18·6 or 19·6	231	44·1	1·00198 or 1·00210
„ 15, 1903 .	35·05	28·2 or 29·2	245	65·2	1·00210 or 1·00218
				Mean. . . .	1·00217

An investigation into the cause of these discrepant values led to the discovery that, owing to the position of the thermometers, which were inserted in holes pierced through the electric furnace, the ordinary formula for stem correction does not give the true temperature of the tube, which was a degree or two higher than the calculated value. Since the vapour density of mercury increases very fast between 200° C. and 300° C. such an error is fatal. Thus at 230° C. a mistake of 1° C. corresponds to an error of nearly 3 per cent. in the result; and at 250° C. to $2\frac{1}{2}$ per cent.

It was also found that sufficient allowance had not been made for the lag of the temperature in the tube behind that shown by the thermometer.

In view of the difficulties involved in eliminating these sources of error, difficulties which would have been increased in dealing with substances whose vapour-pressure at high temperatures has never yet been determined, it was decided to abandon the method for that of the balance. A small glass tube, about 5 millims. in length and ·5 millim. in internal diameter, closed at one end, was weighed before and after a drop of mercury had been introduced into it, and carefully placed in the refractometer tube, which was then evacuated, sealed, and heated till the whole of the substance had evaporated. The amount of mercury required to produce a convenient number of bands was found to be between ·01 and ·02 gramme, a quantity which could be weighed without difficulty to one part in five hundred.

The results obtained by this method showed a most satisfactory agreement. Below are given the details of every experiment performed, except those which were obviously spoiled by the cracking of a tube, or other disaster.

TABLE V.—Refractive Index of Mercury.

Date.	Length of tube.	Volume of tube.	Weight of mercury.	Number of bands observed (temperature falling).	Refractive index of Hg_2.	Remarks.
	centims.	cub. centims.	grammes.			
March 26, 1903	35·05	37·1	·01643	27·15	1·001837	At the third trial. At first the temperature was not taken high enough.
,, 30, 1903	35·05	36·9	·01068	18·45	1·001911	Some uncertainty about the volume of tube. This and the next are doubtful experiments.
,, 31, 1903	35·05	36·9	·01068	18·35	1·001901	Experiment of 30th repeated. Temperature taken at least 20° C. higher than necessary.
April 17, 1903 .	35·15	38·53	·02170	34·9	1·001852	
,, 17, 1903 .	35·15	38·53	·02170	34·9	1·001852	Repetition of preceding.
,, 21, 1903 .	35·15	38·03	·02704	39·0	1·001638	Temperature not taken high enough.
,, 24, 1903 .	35·15	37·05	·00989	16·6	1·001858	
,, 28, 1903 .	35·15	37·0	·01302	21·7	1·001843	
,, 28, 1903 .	35·15	37·0	·01302	21·85	1·001856	Repetition of preceding.
Mean of 8 experiments					1·001864	
Mean of best 6 experiments					1·001850	
Mean correction for the expansion of the volume of the tube					0·000007	
Refractive index of Hg_2 . . .					1·001857	

Of these nine consecutive experiments one was obviously spoiled by failure to raise the temperature high enough to evaporate all the mercury. Of the remaining eight, the 3rd, 5th and 9th were repetitions of the previous experiment, with the same quantity of mercury, and the close correspondence obtained is a fair index of the accuracy obtainable by this method. The weights used varied from ·00989 to ·2170, yet only one of the results departed by as much as $2\frac{1}{4}$ per cent. from the mean, and out of the six best experiments none departed from the mean by as much as 1 per cent. I think that for Hg_2 the value 1·001857 is within 1 per cent. of the true value.

In comparing this result with that of M. LE ROUX it must be remembered that, as was stated above, the latter is calculated without reference to the number of atoms in the molecule, so that the fractional part of the index 1·000556 must be doubled.

This is clear from Table III. given on page 326, where the density of the mercury experimented on is given at the theoretical value required for the boiling-point.

But even after this correction has been made, the discrepancy between the two values is much wider than can easily be explained. It is, therefore, interesting to enquire which of the two results is most in accordance with the value to which the refraction equivalent points.

Gladstone and Dale originally estimated this constant at 20·2 (subject to reservation owing to the anomalous behaviour of its compounds), and the former subsequently reduced it to 19·4. Kannonikoff places it as 19·2. Accepting Gladstone's later value, and comparing it with his value for oxygen (2·8) and the known refractive index of the latter (1·000270), we obtain, by proportion, the value 1871 for the refractivity of Hg_2, a number extraordinarily close to that now found. If, instead of using the refraction equivalents, we compare the indices of the methyl and ethyl compounds of mercury with those of the analogous ethers a similar agreement is obtained.

This evidence, then, corroborates the value obtained by the refractometer, and raises the presumption, which we shall see to be justified in other instances, that the method of Le Roux contains sources of error even greater than he imagined.

Arsenic.

Experiments were made with arsenic, but it was found that this element does not sublime at the temperature at which shellac begins to char. The investigation of this index has, therefore, been postponed until a quartz tube can be procured.

Phosphorus. (Atomic Weight = 31·0.)

Phosphorus was the next element attacked. Here the principal difficulty lay in avoiding oxidation while the substance was being weighed and introduced into the refractometer tube.

Before constant results were attained nine experiments were performed (besides spoiled experiments), of which the details are given below, in order, as in the case of mercury, to corroborate the value afterwards reached, when the sources of error were better understood. In this first series of experiments, the capillary containing the phosphorus was in most cases open to the air during the weighing, and to this cause must be mainly attributed the discrepancies shown.

TABLE VI.—Refractive Index of Phosphorus. Preliminary Experiments.

Date.	Length of tube.	Volume of tube.	Weight of phosphorus.	Bands observed.		Refractive index for P_2.	Remarks.
				Temperature rising.	Temperature falling.		
	centims.	cub. centims.	grammes.				
May 7, 1903	35·00	42·7	·00547	—	37·92	1·00138	
„ 18, 1903	35·15	42·1	·01173	—	73·9	1·00122	
„ 21, 1903	35·00	42·3	·00978	—	61·35	1·00123	
„ 23, 1903	35·00	36·7	·02219	—	150·5	1·00116	
„ 29, 1903	35·00	42·9	·03424	205·9	207·9	1·00121	
„ 30, 1903	35·00	42·9	·03424	—	207·8	1·00121	Repetition of preceding.
June 6, 1903	35·00	35·43	·01505	—	96·2	1·00105	A leaky tube.
„ 10, 1903	34·8	35·5	·00533	41·7	—	1·00130	Not a good experiment. A leak occurred and some red phosphorus afterwards found in the tube.

In the next series of experiments greater precautions were taken. The phosphorus used was freshly prepared, and was free from discoloration. About a quarter of a gramme was cut from the stick under water, rapidly dried on blotting paper in a current of dry CO_2, and placed in a glass tube which ended in an open capillary. Here it was further dried in a current of CO_2 for about a quarter of an hour, when the tube was exhausted and sealed off. The phosphorus was then melted *in vacuo* and freed from impurities by being run into the capillary part of the tube, where a convenient portion, isolated by judicious warming, was sealed off in a length of about 1 centim. The whole operation was conducted in a dark room with the least possible light, and the phosphorus appeared quite clean and transparent. The refractometer tube, after being dried, was filled with CO_2, and the capillary was scratched with a glass knife, weighed, and broken in a current of CO_2. Both halves were instantly dropped into the refractometer tube, and this was immediately exhausted and sealed off. After the experiment, the two halves of the capillary were re-weighed, and the weight of phosphorus used calculated by subtraction. The condition of the phosphorus after each experiment afforded a trustworthy test of its success. If a leak occurred, the phosphorus was found on the sides of the tube in red scales. But if all had gone well, it was seen to be condensed into a colourless transparent bead in one part of the tube. No experiment in which this was not the case was accepted. With these precautions, remarkably constant results were obtained.

Table VII.—Refractive Index of Phosphorus.

Date.	Length of tube.	Volume of tube.	Weight of phosphorus.	Number of bands observed.		Mean.	Refractive index for P_2.	Remarks.
				Temperature rising.	Temperature falling.			
	centims.	cub. centims.	grammes.					
June 23, 1903	34·0	31·23	·03639	288·7	290·7	289·7	1·001191	
,, 25, 1903	34·0	31·23	·00486	36¾	—	—	1·001131	See below.
,, 26, 1903	34·0	31·42	·04974	389	398·6	398·6*	1·001199	*See below. The first reading, 389 bands, gives 1·001178.
,, 29, 1903	34·0	31·26	·00740	58·8	58·5	58·65	1·001185	
Mean of experiments 1, 3, and 4							1·001192	
Mean correction for the expansion of the volume of the tube							·000005	
Refractive index of P_2							1·001197	

In the second experiment some disaster happened when 36¾ bands had passed. The experiment was, therefore, practically spoiled, and the figures are only inserted in the table for the sake of completeness. It does, however, give a value which cannot be less than the true number, so that it is not completely valueless. In the third experiment there is a difference of nearly 10 bands between the upward and downward readings. This may have been due to fatigue on my part, as the experiment involved counting nearly 800 bands, and sitting at the telescope for 2½ hours consecutively, or it may have been due to a rush of bands which I suspected to have taken place as the temperature was rising. The figure chosen is that in which I have most confidence.

The value for P_2, $\mu = 1·001197$, is probably within 1 per cent. of the truth.

Such an index is as far removed from M. Le Roux's value of $\mu = 1·000682$ as that now found for mercury was from his $\mu = 1·001112$, and if we seek confirmation of the refractometer method from the other evidence in our possession we find that the refraction equivalent of P calculated by Gladstone and Dale (18·3) is almost equally far from corroborating either value; for it points to an index of about 1·000880, which is about midway between the present value and that of Le Roux. But, if we turn to a consideration of the refractive indices of those compounds of P which have been measured in the gaseous or liquid state, the results strongly support the new value.

The compounds of P whose refractive indices have been measured are more numerous than those of mercury. From the following table it will be seen that, in the case of PH_3 and PCl_3, whose indices have been measured in the gaseous form, the value now obtained satisfies with great exactness the rule so firmly established that the refractivity of a compound is slightly less than the sum of the refractivities of its components in the free state. In the case of the liquid compounds, where additional uncertainty is introduced by the transformation of the indices by the formula of LORENZ and LORENTZ, the agreement is not so close, but the discrepancies are not abnormal in amount. The substitution of LE ROUX's value would give worse results in six, and that of GLADSTONE in five, cases out of seven.

A comparison of the indices of the triethyl compounds of P and N strongly supports the same view.

TABLE VIII.—Refractive Indices of Phosphorus Compounds.

Compound.	Refractive index.			Refractivity $(\mu - 1)\,10^6$.	Refractivities of components, ($P_1 = 599$).	Sum.	Difference of columns 5 and 7.	Difference per cent.	Observer.
	Gaseous.	Liquid.	Calculated for gas from liquid by LORENZ' formula.						
PH_3	1·000786	—	—	786	$599 + 3 \times 69\frac{1}{2}$	807·5	21·5	− 2·7	DULONG.
PCl_3	1·001730	—	—	1730	$599 + 3 \times 384$	1751	21	− 1·2	MASCART.
PBr_3	—	1·6866	1·002450	2450	$599 + 3 \times 562{\cdot}5$	2286·5	164	+ 7·1	GLADSTONE and DALE.
P_4S	—	2·0661	1·003025	3025	$4 \times 599 + 551$*	2947	78	+ 2·6	BECQUEREL.
P_2O_6	—	1·5405	1·001725	1725	$2 \times 599 + 3 \times 270$	2008	283	− 14·1	THORPE and TUTTON.
$POCl_3$	—	1·4602	1·001715	1715	$599 + 135 + 3 \times 384$	1886	171	− 9·1	ZECCHINI.
$PSCl_3$	—	1·57547 (F.)	1·002281	2281	$599 + 3 \times 384 + 551$	2302	21	− 0·9	NASINI and COSTA.
$P(C_2H_5)_3$	—	1·45799	1·002700	2700	Assuming the additive law, as a first approximation, the value for P_1 is given by the equation $2265 - 149 + (\text{refractivity of } P_1) = 2700$; whence $(\text{refractivity of } P_1) = 584$.				
$N(C_2H_5)_3$	—	1·4003	1·002265	2265					

---

* The value taken for S is that subsequently found. See p. 342.

On comparing the new value with that of nitrogen, the first member of the chemical group to which phosphorus belongs, a very remarkable relation is at once apparent. The refractive index of N_2 for sodium light has been determined by MASCART to be 1·0002973 and by RAMSAY and TRAVERS 1·0002971. Accepting the mean of these observations, it will be seen that the ratio of the refractivity of P_2 to that of N_2 is 4·03; or, in other words, it appears that, to an accuracy of 1 per cent., which is within the limits of experimental error, *an atom of phosphorus retards light four times as much as an atom of nitrogen.*

Sulphur. (Atomic Weight = 32·06.)

The study of the refractive index of sulphur presents comparatively little difficulty, for it is easily obtained pure, and can be weighed and introduced into the tube with facility.

Sulphur, well washed in distilled water to free it from traces of acid, and dried at 100° C., was redistilled *in vacuo.* The distillate was melted and sucked into capillary tubes, forming thin sticks whence a small cylinder of the proper weight was broken off. This could be conveyed into the tube without loss of weight.

Two experiments were found necessary to discover the maximum quantity of sulphur which would be vapourised at the highest temperature available. When this had been done, the results obtained were so concordant that only four experiments were necessary to give a trustworthy value. Of these, the first is the least good. The number of bands observed was only $15\frac{1}{5}$, and the corrections for the "starting" effect were of the order of $\frac{1}{10}$ of this number. Any error in the estimate of this correction, therefore, had a large proportional effect on the result.

In the second experiment the "starting" effect was difficult to judge accurately. I give the figures based on the estimate least favourable to concordant results.

TABLE IX.—Refractive Index of Sulphur.

Date.	Length of tube.	Volume of tube.	Weight of sulphur.	Number of bands observed.		Mean.	Refractive index for S_2.
				Temperature rising.	Temperature falling.		
	centims.	cub. centims.	grammes.				
July 9, 1903 . .	34·05	40·650	·00273	15·2	15·0	15·1	1·001111
Sept. 18, 1903. .	34·05	40·642	·00511	28·05	28·75	28·45	1·001118
„ 23, 1903. .	34·05	40·590	·00845	46·0	46·1	46·05	1·001093
„ 26, 1903. .	34·05	40·590	·00652	34·55	34·95	34·75	1·001068
Mean							1·001097
Mean correction for the expansion of the volume of the tube . .							0·000004
Refractive index for S_2							**1·001101**

Table IX. gives the details of the experiments. Having regard to the smallness of their number, I consider that the error in this determination may equal, though it probably does not exceed, $1\frac{1}{2}$ per cent.

If, as in the case of P and Hg, we try to verify this value by a comparison with the indices of compounds of sulphur and of its refraction equivalent, we are met by anomalies which show that no single value of the refractivity of sulphur will satisfy all cases.

Table X. gives the indices and refractivities of the compounds of sulphur, the refractivities of all of whose constituents are known. It will be seen that the refractivities which must be assigned to S, in order to satisfy the additive law, vary widely from the value of 551 here given for S_1. In SO_2, H_2S, SO_2Cl_2, and notably in H_2SO_4 and SO_3HCl, a smaller value would best accord with the facts. In $SOCl_2$, $PSCl_3$, P_4S, the value 551 would fit in excellently. In SCl_2, S_2Cl_2 a value slightly larger, and in CS_2, whose refractivity is 1476, a much larger value is required; for the highest contribution we can expect from C. is 250, which would leave 610 to be accounted for by each of the sulphur atoms. Finally, the smaller of the two refraction equivalents calculated by GLADSTONE for S (14·1), when compared with that of O (2·8), would point to a value as high as 680.

All that can safely be concluded from these highly interesting anomalies is that the refractive power of sulphur varies greatly, according to the nature of the compound which it forms, and that the value now found is not far from the mean round which the discrepant values are grouped.

In the periodic table of the elements, oxygen occupies, with regard to sulphur, the same relative position that nitrogen does with regard to phosphorus, and argon to neon. And, if we compare the refractive powers of the first pair, it is astonishing to find that their ratio is, within the limits of experimental error, the same as that found for the other two.

The most recent determinations of the index of oxygen for sodium light are 1·002702 (MASCART), 1·0002716 (LORENZ), 1·0002702 (RAMSAY and TRAVERS).

If we accept the value in which two of these researches concur, and compare it with the value 1·001101 now given for S_2, it appears that the ratio of their refractivities is 4·08 against 4·03 found for N and P and 4·13 for Ne and A. The agreement is 1 per cent. worse in the present case than in that of P, perhaps owing to the fewness of the experiments, or possibly to the wide dispersive power of sulphur. But the concordance is too close to be accidental; and it may therefore be said that, at least to a first approximation, *an atom of sulphur retards light four times as much as an atom of oxygen.*

TABLE X.—Refractive Indices of Sulphur Compounds.

Compound.	Refractive index.			Refractivity $(\mu - 1) 10^6$.	Refractivities of components, S = 551.	Sum.	Difference of columns 5 and 7.	Difference per cent.	Observer.
	Gaseous.	Liquid.	Calculated for gas from liquid by LORENZ' formula.						
SO_2	1·000702	—	—	702	551 + 270	821	119	− 14·3	MASCART.
H_2S	1·000619	—	—	619	551 + 139	690	71	− 10·2	,,
SCl_2	—	1·57806	1·001394	1394	551 + 768	1319	75	+ 5·7	COSTA.
S_2Cl_2	—	1·65298	1·001974	1974	1102 + 768	1870	104	+ 5·6	,,
$SOCl_2$	—	1·5271	1·001482	1482	551 + 768 + 135	1454	28	+ 1·9	NASINI.
SO_2Cl_2	—	1·44372	1·001442	1442	551 + 768 + 270	1589	147	− 9·3	PAWLEWSKY.
H_2SO_4	—	1·4351	1·00937	937	551 + 139 + 540	1230	293	− 23·8	BADEN POWELL.
SO_3HCl	—	1·4371	1·001162	1162	551 + 405 + 69 + 384	1409	247	− 21·1	NASINI.
P_4S	—	2·0661	1·003025	3025	*2396 + 551	2947	78	+ 2·6	BECQUEREL.
$PSCl_3$	—	1·57547	1·002281	2281	599 + 551 + 1152	2302	21	− 0·9	NASINI and COSTA.
CS_2	1·001476	—	—	1476	1102 + X	—	—	—	MASCART.

---

* The value for P is that given on p. 338.

Work on Fluorine.

In a letter to 'Nature,' of November 13th, 1902, it was pointed out that, if there were any simple relation between the refractivities of the elements of the different chemical groups, it should be found to exist also in the case of fluorine, whose refractivity should bear to that of chlorine the same ratio of 1 to 4 which the refractivity of neon bears to that of argon.

With the object of testing this prediction I have spent some time in attempting to measure the refractive index of fluorine in the gaseous state; but I regret that the experimental difficulties due to the active nature of this element have not yet been completely overcome. Sufficient experience of the nature of these difficulties has, however, been gained to promise the hope of success in the near future.

All that can at present be said is that the results given by two of the most promising series of experiments are not inconsistent with the value predicted.

In February, 1904, I visited Paris, and attempted to measure the index of the gas by letting it flow through a hollow prism of copper, provided with plates of fluor spar. By the kindness of M. MOISSAN, of whose great hospitality and generosity I desire to render the most cordial acknowledgment, I was able to command a stream of fluorine, prepared for me by the skill of his coadjutor, M. VITEAUX, to whom also I owe my most sincere thanks. The gas was allowed to displace the air in the prism till the refractive index reached a minimum, and the deflection of the image of a bright slit was read on a micrometer placed in the focus of a lens of long focal length. The results obtained were not always concordant, and, in the light of subsequent experiments, indicate that the air was never wholly displaced. However, the best experiments gave two concordant values of $\mu = 1\cdot000226$ and $1\cdot000225$, and, since the index of F is certainly lower than that of all other gases except H, He, and Ne, it seems probable that this value is somewhat higher than the index of the pure gas.

Experience shows that a fair guess can be made at the refractive index of an element by comparing the index of a gaseous compound which contains it with that of another compound in which an element of known refractivity is substituted. With this object I measured the index of methyl fluoride and compared it with that of methane. I have to thank Professor NORMAN COLLIE for the loan of a specimen of methyl fluoride of very great purity. Its index, determined in a JAMIN's refractometer, was ascertained to be $\mu = 1\cdot000449$.

The index of CH_4, as determined by M. MASCART, is $\mu = 1\cdot000441$.

Thus, the substitution of an atom of fluorine for one of hydrogen has raised the index by $\cdot000008$, and the inference is that the refractivity of F_2 is probably about 16 higher than that of H_2. Taking the latter as equal to 139, we obtain for F_2, approximately, $\mu = 1\cdot000155$.

If these inferences are justified, we may believe that the index of F_2 is somewhere between $1\cdot000226$ and $1\cdot000156$; a value which is, at least, not inconsistent with that of 1·000192, which corresponds to a retardation of light one fourth as great as that caused by chlorine, whose index is 1·000768. But the experience of previous investigations, and in a special degree of the present work, has shown that no estimate of the refractivity of an element based on the behaviour of its compounds can be relied upon to give a value within 10 or 20 per cent. of the truth; and nothing but actual measurement of the gaseous index can finally settle the question.

In collaboration with Mr. E. B. PRIDEAUX I am at present engaged in further efforts towards this end.

In this connection it is interesting to recall the previous attempts to estimate the index of fluorine. GLADSTONE and DALE placed the refraction equivalents of F and Cl at 1·4 and 9·9 respectively, and this would point to a refractive index of only 1·000108 for F_2. In 1886 G. GLADSTONE estimated the refraction equivalent to be between 0·3 and 0·8. In 1891, Dr. J. H. GLADSTONE and G. GLADSTONE, from a study of all the fluorine compounds then available, placed it at slightly less than 1·0.

Since that date a number of carbon compounds containing one or more atoms of F have been examined in the liquid state. A comparison of their indices shows that, in some cases, a value for the refractivity of F_2 a little higher than that of H_2 (139), in others a little less, would best satisfy the data. Recently Messrs. MOISSAN and DEWAR made an estimate based on the appearance of liquid fluorine. They judged the density of the liquid to be about 1·14, and its index to be probably higher than that of liquid air, which is 1·205, and not far from that of amber, which is stated to be 1·55.*

Calculating the value of the index of the gas from these data by means of LORENZ' and LORENTZ' rule, we find that if the index of liquid F is 1·2, the index of the gas would be 1·000145, and that 1·3 gives 1·000209 and 1·4 gives 1·000246. These figures, then, so far as they go, tend to confirm the probability that the refractivity of F is not far from one fourth that of Cl.

Relative Refractivities of the Elements.

The method of refraction equivalents has never been sufficiently accurate to give any information of great value with regard to the relative refractivities of the elements, and the number of elements whose index has been measured in the free state has hitherto been too small to admit of comparisons.

But, with the addition of the five inert gases and of Hg, P and S, it is impossible to resist making a guess at the laws involved, scanty though our data still remain. Table XI. (p. 346) shows some of the elements in the periodic form, and the refractivities of all those whose indices have been measured in the gaseous state. For the sake of simplicity the numbers are rounded off.

---

* 'Proc. Chem. Soc.,' XIII., 1897, p. 185.

TABLE XI.

H 139	—	—	—	—	—	—	He $139 \times \frac{1}{2}$
Li	Be	B	C	N 297	O 270	F	Ne 139 × 1
Na	Mg	Al	Si	P 297 × 4	S 270 × 4	Cl 192 × 4	A 139 × 4
K	—	—	—	—	—	Br 192 × 6	Kr 139 × 6
Rb	—	—	—	—	—	I 192 × 10	X 139 × 10
Cs	—	—	—	—	—	—	—
—	Hg 1857	—	—	—	—	—	—

The most obvious fact shown by this table is one which the study of the refraction equivalents had long ago made familiar, *i.e.*, that in each family of elements the refractivity increases with the atomic weight, though not in simple proportion to it. It is true that the existing figures for the refraction equivalents show many exceptions to this rule; but the figures themselves are so untrustworthy that anomalies do not destroy the general effect of the evidence.

The second, and perhaps more interesting, point is that the refractivities of the different members of the same chemical family are, within the limits of experimental error, related in the ratios of small integers. This fact, observed first in the family of the inert gases, is equally true in that of the halogens, and, if the present results are approximately correct, is now shown to exist between the two first members of the families of O and N respectively.

The case then stands thus:—The indices of fourteen elements have been measured in the gaseous state.* Of these, two, mercury and hydrogen, are not related to any others whose indices have been determined. The remaining twelve all conform to the rule.† The probability that these coincidences are fortuitous is small. But if they are not, the extreme simplicity of the relations raises the hope that some fundamental property of matter may be involved.

If we attempt to go beyond the elements whose indices have been determined in the free state and enquire how far the refraction equivalents lend support to the

---

* I do not reckon arsenic, since M. LE ROUX himself did not place much reliance on his result, and the present enquiry renders it still more dubious.

† It is a strange fact that the index of H_2 is practically identical with that of Ne_2, but whether this is more than a pure chance it would be hazardous to conjecture.

hypothesis of simple relationships running through every family of elements, it must be admitted that the figures are not encouraging.

The most hopeful series is that of the alkali elements, in which we find that the constants for K, Rb and Cs are 7·85, 12·1 and 19·2, numbers which stand very nearly in the relation of 2, 3 and 5; but lithium and sodium do not show any tendency to fall into their places, and none of the other series of elements promise any better success. It must, however, again be repeated that the refraction equivalents are often misleading, so that an unpromising appearance ought not to daunt us.

The third point which is remarkable in the relative refractivities of the elements is their connection with the valency. In the periodic arrangement of the elements, N, O, and Ne are followed, respectively, by P, S, and A, and the refractivity of each of the latter set is four times that of each of the former. These, therefore, are, probably, in some sense homologous elements, and we may consider together the series Ne, O, N, and A, Cl, S and P. In the latter set we find that A, with the highest atomic weight, but zero valency, retards light least, and that, as we pass to Cl, S, and P, the refractivity increases with the valency, in spite of the decrease in atomic weight. The same thing occurs in the series Ne, O, N; and here it is remarkable that the refractivity of carbon is, in all probability, even greater than that of nitrogen, being at least 320 for C_2, and probably as high as 360.

So far as can be judged from the scanty knowledge we possess, the retarding power diminishes from this point as we move across the table from right to left, that of Li being less than that of carbon. But the case of boron presents extremely interesting features.

GHIRA[*] has measured the indices of BCl_3 and BBr_3 in the liquid state, and the following table shows the values of the refractivity of boron which can be inferred from his results, on the assumption that the additive law for compounds holds exactly.

TABLE XII.

Substance.	Refractive index.		Refractivity $(\mu - 1)\,10^6$.	Refractivity of the halogen.	Refractivity inferred for B_1.
	Liquid.	Calculated for gas by LORENZ' rule.			
BCl_3	1·424 approx.	1·001420	1420	3×384	268
BBr_3	1·546 „	1·002025	2025	3×562	338
				Mean	303
				Mean for B_2 . . .	606

---

[*] 'R. Accad. Lincei Rendiconti,' 1893, vol. 2, sem. 1, p. 312

These two values are widely different, but both are greater than the highest refractivity which it is ever necessary to attribute to carbon. The inference is, either that the index of boron is actually higher than that of carbon, or, that the presence of boron has the effect of increasing the retarding power of Cl and Br in an abnormal degree. It is difficult to say which of these alternatives is the more interesting; and the determination of the indices of BCl_3, BBr_3, and BH_3, in the gaseous state, ought to yield results of the highest importance.

This rule, that increased valency means increased refractivity, is no doubt closely connected with GLADSTONE'S observation that, when an element, such as iron, forms two compounds, that in which it has the highest valency has the highest refracting power, and the allied fact that a double or treble bond is accompanied by increased refracting power in the compound in which it occurs. The problem is one of great interest and is yet unsolved.

Beyond the bare fact that the refractivity does increase with the valency it is difficult to go at present. I have tried, but in vain, to guess the law which connects the refractivities of A, Cl, S, and P (139, 192, 270, 297). It is easy to find specious relations between two or three members of the series, but, until we know the indices of the alkali elements, and can make a nearer approximation to the true values for carbon, boron, and silicon, the data are insufficient, and speculation is useless.

Nor have I been more fortunate in my endeavours to find a meaning for the numbers, 1, 2, 8, 12, and 20, which express the ratios between the refractivities of the different members of the inert family of gases.

CLAUSIUS has shown that, on the assumptions of the electromagnetic theory of light, if the molecules of gaseous matter are perfect spheres, conducting electricity, in a non-conducting medium, the refractivity of the gas is proportional to the fraction of space occupied by the molecules. And if, for molecules, we put electrons, it would follow that the sum of the volumes of the electrons (or possibly their number), in similar elements, are in the ratios of small integers. But this theory throws no light on the peculiar numbers actually observed.

Indices of Compounds.

From the tables given above, it will be seen that the determination of the indices of S and P enables us to add 15 compounds to the slender list of those in which the refractive indices of all the components in the free state are known. Of these, 11, viz., PBr_3, P_4S, P_2O_6, $POCl_3$, $PSCl_3$, $SOCl_2$, SCl_2, S_2Cl_2, SO_2Cl_2, H_2SO_4, SO_3HCl, have had their indices measured in the liquid state; and 4, viz., SO_2, H_2S, PCl_3, and PH_3, in the state of gas. It might have been expected that this addition to the available *data* would have afforded some clue to the relation of the indices of compounds to those of their constituents, but I have been unable to find any; and I doubt if the problem will be solved till we are in possession of the indices of a large number of simple compounds, determined in the gaseous state to a degree of accuracy higher than that which can be claimed for the existing determinations.

The list of the obligations which I desire to acknowledge is a long one. I have to thank Professor TROUTON for his kindness in admitting me to the Physical Laboratory of University College, London, and in placing at my disposal all the resources at his command. To him, to Assistant Professor A. W. PORTER, to Sir WILLIAM RAMSAY, and to every Member of the Chemical and Physical Staff of University College, I owe a debt of thanks for their unwearying kindness and invaluable help. I have already expressed my obligations to M. HENRI MOISSAN and his staff, for their assistance in the work on fluorine. To Mr. HILGER, and after his death, to Mr. TWYMAN, I am deeply indebted for the interest they have shown in the preparation of the refractometer tubes, and for the skill and accuracy of their workmanship. Finally, I have great pleasure in again expressing my cordial thanks to the Government Grant Committee of the Royal Society for the contribution they have made towards the expenses involved in the work.