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THE REFRACTION AND DISPERSION OF AIR FOR THE VISIBLE SPECTRUM

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1. Introduction and summary

(*a*) *Note on previously recorded values of the refractive index of air.* For many centuries astronomers have recognized the effect that the refraction of the earth's atmosphere has upon observations of the positions of celestial bodies. From the time of Tycho Brahe, when astronomical technique became sufficiently refined for the purpose, attempts have been made to apply corrections for the deviation of light in its passage through the earth's atmosphere, and ultimately, in 1805, Delambre (1806) determined, by comparing a large number of astronomical observations, a value of the refractive index of atmospheric air for white light. The first accurate laboratory determination was made about the same time by Biot and Arago (1806), who measured the deviation of white light passing through air enclosed in a hollow glass prism.

In 1857 Jamin (1857*b*) made his original application of the methods of interferometry to the measurement of the refractive index of a gas. The increased accuracy obtainable by the use of the principle of the Jamin refractometer enabled Ketteler (1865) to determine the refractive indices of air for the red, yellow and green lines in the visible spectra of lithium, sodium and thallium respectively, and thus to make some of the earliest measurements of the dispersion of air.

Since the middle of the nineteenth century the need for more accurate information on the refraction and dispersion of gases, arising mainly from a desire to obtain data for the elucidation of problems concerned in the propagation of light through transparent media, has provided a continuous incentive to researches on the subject by physicists. Apart from those investigations on air carried out for the special requirement of correcting spectroscopic observations, air has been more frequently chosen than any other gas as the material for investigation, no doubt for the reason that, although it is a mixture which does not lend itself so well as a pure gas to the determination of fundamental physical relationships, a knowledge of the refractive index of air is of great importance from a practical standpoint. Summaries of earlier work on the refraction and dispersion of air have already been published by other authors, notably by Meggers and Peters (1918–19), and by Pérard (1934), and Tilton (1934) has collected for the period 1857–1932 the results of forty different determinations of the refractivity of dry air for sodium light. The general average value of the refractivity, at 0° C. and 760 mm. pressure, in Tilton's collection is

$$(n_D-1)\,10^6 = 292{\cdot}5_4,$$

where n_D is the refractive index for sodium light. The total range exhibited by the values is within the limits of $\pm 0{\cdot}75\,\%$ of the value of the general mean, corresponding to ± 2 parts in 10^6 of the value of the refractive index. Apart from the earliest work considered in these results, such a variation cannot be regarded as satisfactory, especially as most observers claim limits of experimental accuracy which are only a small fraction of this range.

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(*b*) *New determinations for metrological purposes.* When formal sanction was given by the Seventh General Conference on Weights and Measures (Comité Int. 1927) to the proposal that determinations of length might be made, as an alternative to direct reference to the metre, in terms of the wave-length of the red line of cadmium, the attention of metrologists became particularly directed to the variations in recorded values of the refractive index of air for the visible spectrum. The reason for this is evident from the fact that the relationship which had temporarily to be adopted was one between the metre and the wave-length in air under certain standard conditions. Since the wave-length of a radiation varies in inverse proportion to the refractive index of the medium through which the radiation is transmitted, a possible variation of about ± 2 parts in 10^6, such as that shown in the recorded values of the refractive index of air, was obviously disturbing, and in 1931 the International Committee on Weights and Measures agreed that further precise measurements of the refractive index of air were required (Comité int. 1931). It may be pertinent to mention here that the present authors (1934, p. 181) have already advanced certain tentative proposals for the adoption of *ideal* definitions of the units of length in terms of wave-lengths *in vacuo*, rather than wave-lengths in air, but this would not avoid the practical necessity for more accurate information on the refraction of air, since it is convenient for most ordinary purposes to make optical measurements in air, even though reference to the vacuum condition is preferred for the standard unit.

Pérard (1934), at the Bureau International des Poids et Mesures, had already, in 1924, completed an investigation of the refractive index in the visible spectrum of dry, CO_2-free air, at temperatures from 0 to 100° C. and at ambient atmospheric pressures. Kösters and Lampe (1934), of the Physikalisch-Technische Reichsanstalt, have since given the result, with no experimental details, of a similar investigation, but with temperatures confined near to 20° C. The agreement between the results of these observers at 20° C., for the value of the refractive index in the region of visible wave-lengths between 0·45 and 0·65μ, is on the average within 1·4 parts in 10^7, although the dispersion curves are of slightly different shape. Furthermore, the calculated values of n_D at 0° C. and 760 mm. are within ± 1 part in 10^7 of the general average value of all observers within the period 1857–1932.

At the National Physical Laboratory investigation of the refraction and dispersion of air was postponed until after the completion of definitive measurements of the yard and metre (1934) in terms of wave-lengths of light, which had also been undertaken partly as a result of an earlier decision of the International Committee in 1923. In the course of this work values of the refractive index of air for the red radiation of cadmium were indirectly derived from the optical measurements of length, from which a value could be deduced for n_D at 0° C. and 760 mm. which was also in close agreement with the general average value of all observers between 1857 and 1932. Incidentally it also became evident that the wave-length comparator, designed and constructed for the optical measurements of length, could well be utilized, with slight modification and

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the addition of some necessary auxiliary apparatus, to determine absolute values of the refractive index of air for the visible spectrum, by means of an interferometric method differing somewhat in principle from any which had been previously employed for this purpose, and which promised to afford results of high precision.

In brief, the method employed makes use of Brewster's fringes, or the fringes of superposition, produced in a beam of monochromatic light transmitted by two Fabry-Perot étalons of nominally equal lengths placed in series. Since the étalons used in the wave-length comparator are of an enclosed, airtight type, one of them can be filled with air under known and controlled conditions of temperature, pressure and composition, and the other evacuated; if now the former étalon is also exhausted the Brewster's fringes will be displaced, the amount of displacement measured in fringes being equal to the change of retardation in this étalon owing to the withdrawal of the air. Allowance having been made for the small alteration in the dimensions of this étalon consequent upon evacuation, the refractive index may easily be calculated if the length of the étalon is known. With the étalons used in this investigation the displacement for 1 atm. is of the order of 700 fringes in mercury green light, and this may be measured by photographic and photometric means to an average accuracy of $\pm 0{\cdot}01$ of a fringe separation. An accuracy of ± 1 part in 70,000 in the measurement of refractivity, corresponding to an accuracy of measurement of the refractive index of ± 1 part in 5×10^9, should therefore theoretically be attainable, if errors in the measurement of temperature and pressure and the uncertainty of the composition of the air could be entirely neglected.

(*c*) *Relations between refractive index and density of transparent media.* Before proceeding to outline the various aims of this new investigation it is necessary to discuss two important problems concerning the transmission of light through a transparent medium, namely, the manner in which the density of the medium affects the refraction of light, and the nature of the variation of refractive index of the medium with wave-length or frequency. The first of these problems has for long been the frequent subject of investigation. Hauksbee (Ivory 1823) is reputed to have first determined by experiment that air refracts light in proportion to its density, and many of the famous mathematicians, such as Bernoulli, Euler, Lagrange and Laplace, made theoretical investigations in order to derive the differential equation of the path of light through the earth's atmosphere and thus supply a basis for the compilation of tables of corrections for the astronomical refractions.

It is well known that, at various times, three important expressions have been proposed for the relation between the refractive index n, for a particular wave-length of radiation, and the density d of a given transparent body. These expressions, in historical order, are:

$$\text{Newton-Laplace}\quad (n^2-1)/d = \text{constant}, \tag{1·1}$$

$$\text{Gladstone and Dale}\quad (n-1)/d = \text{constant}, \tag{1·2}$$

$$\text{Lorenz-Lorentz}\quad (n^2-1)/(n^2+2)\,d = \text{constant}. \tag{1·3}$$

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A fourth empirical relation, which is frequently quoted in the literature on the subject on the authority of Magri (1905), will be shown in a later section of this paper to be based on a curious error, for which Magri himself appears to be responsible. In reality, his results supply an important confirmation of the third expression quoted above, and Lorentz (1909) himself has quoted them for this purpose, though without reference to the error in Magri's paper which he has tacitly corrected.

Expression (1·1) was found by Newton to be reasonably true for many liquids when the temperature was varied, and was partially based on deductions from the emission theory of light. Laplace inferred the same expression from theoretical considerations based on the form of the undulatory theory accepted in his time. Jamin (1856, 1857*a*), as a result of experiments on water and its vapour, considered that the law did not hold when a change of state occurred, and since his time it has come to be regarded merely as an empirical approximation.

Better agreement with the experimental facts is obtained with the empirical expression (1·2), which was propounded by Gladstone and Dale (1858, 1863) as the result of experiments on water and carbon disulphide at different temperatures. Sutherland (1889) has attempted to give a theoretical basis for this relation, though without much success.

The third relation is probably the most interesting both theoretically and practically. It was independently derived by L. Lorenz (1880), of Copenhagen, and H. A. Lorentz (1936), of Amsterdam, from entirely different theoretical grounds, the former by considering the passage of light through ponderable media consisting of spherical molecules immersed in an ether having the properties of an elastic solid, and the latter from his own theory of electrons considered in relation to Maxwell's system of equations for the electromagnetic theory of light. Lorenz, Prytz and others have found it particularly successful in correlating the facts when a liquid passes to the gaseous state.

In general, the experimental comparison of the three relations in the case of gases at normal densities is not so easily made as it is in the case of liquids, although a considerable amount of research has been devoted to the subject owing to the ease with which the density of a gas may be varied by alterations of temperature and pressure. The reason for this difficulty is that the refractivity of gases at normal densities is small, and the first and third relations quoted above therefore reduce, as a first approximation, very closely to the same simple form as the second, as has been shown by Lorentz (1936, **2**, 88).

(*d*) *Temperature-pressure relations affecting the refractivity and density of gases.* A direct consequence of the close proportionality between refractivity and density in the case of gases, even at moderately high densities, is that variations of refractivity with temperature and pressure should closely correspond with those of density under the same influences. In fact, the departures of gases from the well-known laws of a perfect gas may very well be investigated by refractivity measurements, as will be indicated later in this paper.

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It is of interest to compare the results of previous experimental work on the changes of refractivity and density of air under the influence of temperature and pressure variations. The usually accepted value for the temperature coefficient of volumetric expansion of air, under a constant pressure of 1 atm., is 0·003672 per 1° C., within the range of normal variations of atmospheric temperature. This value was determined by Chappuis (1907) with the constant-pressure air thermometer, and the value of 0·00367 has been found by Benoît (1889) for the temperature coefficient of refractivity of dry air between 0 and 80° C. and at ambient pressures. Among other values which have been determined for the temperature coefficient of refractivity may be mentioned that of 0·003689 derived by Gylden (1866, 1868) from astronomical observations, while laboratory determinations show variations from 0·00382 (Mascart 1877) down to 0·00311 (v. Lang 1874). The corresponding value found for the temperature range 12–31° C., and at 1 atm. pressure, in the investigation to be described in this paper, is 0·003674 ±0·000002.

As regards the relation between the refractivity of gases and their pressure at constant temperature, Mascart (1877) found experimentally for pressures up to 8 atm. that the following expression closely represented his results:

$$(n-1) = Kp(1+\beta p), \tag{1·4}$$

where K and β are constants and p is the pressure. He also found that the experiments of Regnault on the compressibility of gases within the same pressure range could be accurately represented by

$$d = \Delta p(1+\delta p), \tag{1·5}$$

where Δ and δ are constants. The undoubted correspondence (Lorentz 1936, **2**, 89) existing between the values of β and δ, as determined for several gases respectively by Mascart and Regnault, was accepted by Mascart as proof that within the limits of experimental error the refractivity of a gas at constant temperature is sensibly proportional to its density.

The comparatively small discrepancies between the values of β and δ, which were ascribed by Mascart to experimental error, were mostly in the sense $\beta > \delta$, and it has been pointed out by Lorentz (1936, **2**, 89, 90) that β should theoretically be slightly greater than δ, a conclusion which is in harmony with Mascart's findings.

Opladen (1927) has given a collection of values of β for air as determined by different observers, and it is interesting to mention that for pressures over 1 atm. general agreement with the results of Mascart is found, whereas for pressures under 1 atm. large discrepancies exist and all values given are greater than any determined at higher pressures. This has led Posejpal (1917, 1921) to suggest that there is a relation between β and pressure. The results obtained in the investigation to be described herein, for pressures from about 1 atm. downwards, do not confirm Posejpal's suggestion, for the value found for β is within the range of values determined from work at higher pressures by other observers.

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Berthelot (1907) has made an investigation, based partly on theoretical and partly on empirical grounds, of the characteristic behaviour of gases at low pressures. Using as theoretical basis the Van der Waals' equation of state as modified by Clausius, and then introducing a further modification, derived from the experimental facts, concerning the departures of gases from Boyle's law at low pressures, he obtains a general expression for the relation between δ (which is, in effect, a measure of the departure of gases from Avogadro's law) and temperature. It will be seen in a later section of this paper that the value of β determined for air at pressures from 1 atm. downwards is also found to vary with temperature, both the magnitude and the sense of the variation agreeing reasonably well with the expectations from Berthelot's theory. Even better agreement is found with the experimental results of work on the compressibility of air as obtained by Rayleigh (1905), Berthelot and Sacerdote (see Berthelot 1907), and Holborn and Schultze (1915). This result was obtained by applying what we believe to be a new method of reducing the observations of refractivity at various temperatures and pressures, based on the relation between density, temperature and pressure derived from Berthelot's representation of the characteristic behaviour of gases at low pressures.

(*e*) *Dispersion of transparent media.* As regards the dispersion of transparent media the earliest relation proposed for the variation of refractive index with wave-length was the Cauchy equation,

$$n = a + b\lambda^{-2} + c\lambda^{-4} + \ldots,$$

in which a, b, c, etc., are constants and λ is the wave-length. Modern determinations of the dispersion of air for the whole visible spectrum can be accurately represented by an interpolation equation of the Cauchy type having three terms on the right-hand side, thus:

$$(n-1) = a_1 + b_1\lambda^{-2} + c_1\lambda^{-4}, \tag{1·6}$$

in which values of λ in air or *in vacuo* may be used according to convenience, and a_1, b_1, and c_1 are constants.

The work of Sellmeier, Ketteler and Helmholtz on the mechanical theory of dispersion led to the relation generally known as the Sellmeier equation:

$$(n^2-1) = \Sigma[D_0/(\nu_0^2-\nu^2)], \tag{1·7}$$

in which the D_0 terms of the series are constants, ν is the frequency of the incident radiation, and the ν_0 terms are frequencies of lines in the absorption spectrum of the dispersing medium, one or more of which must lie in the ultra-violet region in the case of transparent bodies. This equation can be reduced, in the case of air for the visible region, to the form

$$(n^2-1) = a_2 + b_2\lambda^{-2} + c_2\lambda^{-4}.$$

The Lorenz-Lorentz expression (1·3) is in reality a particular case of the general dispersion equation developed by Lorentz (1936, **3**, 22), which is

$$\frac{n^2-1}{n^2+2} = \Sigma\tfrac{4}{3}\pi c^2 N\frac{e^2}{m}\frac{1}{\nu_0^2-\nu^2}, \tag{1·8}$$

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where c = velocity of propagation of light *in vacuo*,

N = number of molecules per unit volume of the medium, and is therefore proportional to the density,

e, m = electronic charge and mass respectively.

For a given medium, the right-hand side reduces to the same form as the Sellmeier equation, so that

$$(n^2-1)/(n^2+2) = \Sigma[D_0'/(\nu_0^2-\nu^2)],$$

where the D_0' terms of the series are constants. For air in the visible spectrum, this equation can be reduced to the form

$$(n^2-1)/(n^2+2) = a_3+b_3\lambda^{-2}+c_3\lambda^{-4}.$$

As the present investigation was concerned only with the limited range of visible wave-lengths 0·44–0·64μ, which is well removed from the position of the absorption bands of air in the extreme ultra-violet region, interpolation equations expanded in the Cauchy form with three terms were found to give a completely satisfactory expression for the dispersion of air.

(*f*) *Effects of composition of the air upon refraction measurements*. The question of the relation between refractive index and density of air is rendered additionally difficult owing to the fact that air is a mixture of many gases. Certain chemical data relating to the constancy of composition of the atmosphere at the earth's surface, apart from the proportions of water vapour and carbon dioxide present, appear to indicate that appreciable variations of density may be found in different samples, and this might be expected to lead to similar variations in refractive index, but it is shown later in this paper that the refractivity of different samples of air is remarkably constant.

It is usually assumed that a normal amount of 0·03 % by volume of CO_2 is present in the open air and also in well-ventilated rooms, but in badly ventilated rooms this proportion may be considerably exceeded. However, the total uncertainty from this cause, in those previous investigations where CO_2 was not eliminated, is not likely to exceed 1 or 2 parts in 10^7 of the value of the refractive index. The influence of water vapour has been generally recognized in determinations of refractivity of air, and the moisture removed by the usual chemical absorption methods. It is, however, frequently desired in spectroscopic and metrological work to know what changes are produced in the refractive index of air with the normal variations of humidity. The information available for this purpose is very meagre, and the opportunity has been taken in this investigation to obtain information on the humidity factor by observing the effect of adding known amounts of water vapour to dry, CO_2-free air.

A very interesting suggestion has been made by Tilton (1933, 1934) to account for the variations between the values of the refractive index of dry air, as measured by different observers at different dates. From an examination of the forty absolute determinations made within the 75-year period between 1857 and 1932, Tilton states

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that he finds evidences of systematic variations and a probable correlation between refractivity and sunspot activity, the relation found being of a periodic nature corresponding to the magnetic cycle of about 23 years. The explanation given is that, since the turbulence of the earth's atmosphere is already believed to be broadly related to sunspot activity, the average density of air (and therefore refractivity) at the earth's surface may be expected to vary with the cycle of sunspot activity owing to changes in the degree of mixing of the various components of air on this account. No evidence of this correlation has been obtained from the present investigation, the experimental work of which was carried out at various times during the period, from the summer of 1935 to the spring of 1937, when sunspot activity was probably increasing at its maximum rate for the present cycle. Indeed, during this period, the value of the refractive index of dry, CO_2-free air was constant within the limits of experimental error, which, from internal evidence obtained from the determinations, would appear to be closely ± 1 part in 10^8 of the magnitude of the refractive index.

(*g*) *Aims of the present investigation*. The aims of this new investigation on the refraction and dispersion of air were:

(i) To obtain reliable values of the refractive index of dry, CO_2-free air at temperatures and pressures within the range of normal variations of atmospheric conditions, the measurements being confined to eight evenly distributed wave-lengths within the range ($\lambda\, 0{\cdot}44\mu$ to $\lambda\, 0{\cdot}64\mu$) of the visible spectrum usually employed in metrological work.

(ii) To deduce from these values a general interpolation equation for the dispersion of dry, CO_2-free air which will enable a definitive value of the refractive index to be calculated for any radiation within the range of wave-lengths mentioned in (i), and for any temperature and pressure within the range of ambient atmospheric conditions.

(iii) To investigate the relation between the refractive index and density of dry, CO_2-free air at temperatures within the range 10–30° C., and pressures from about 100 to 800 mm. of mercury.

(iv) To determine the effect of water vapour upon the refraction and dispersion of air.

(v) To test the suggestion advanced by Tilton that the refractivity of dry air and sunspot activity may be correlated.

The succeeding sections of this paper give an account of the experimental methods employed and of the results obtained in the execution of these aims, together with a discussion of the relation between refractive index and density of air in its association with the characteristic behaviour of gases at normal temperatures and at pressures from about 1 atm. downwards.

2. METHOD

The principle of the interference method used for refractivity measurements in this work was first described by Fabry and Buisson (1919) and Fabry (1923) for the particular purpose of comparing the optical lengths of étalons, and the present authors have

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already employed it for this purpose in optical measurements of the fundamental units of length (Sears and Barrell 1932, 1934).

Fig. 1 is a diagram which indicates how the method of Fabry and Buisson is applied to the measurement of the refractive index of air. A and B represent two Fabry-Perot étalons of approximately equal lengths, l_A and l_B respectively, each étalon consisting of two optically flat glass plates with their semi-silvered surfaces (indicated by thickened lines in the figure) arranged parallel to one another. In the manner usually adopted in Fabry-Perot étalons, each plate is cut slightly wedge-shaped, with the same angle (of the order of 2–5 min.) between the plane surfaces, and each pair is disposed so that the effect of the small wedges upon the transmitted light is compensated; this arrangement avoids the confusion which would arise from having four mutually parallel surfaces in each étalon. Étalon A is arranged for convenience with its partially reflecting surfaces normal to the optical axis of a telescope, the object lens O of which is seen at the left of the figure, while étalon B is mounted in such a manner that the normal to its partially reflecting surfaces can be inclined through small angles in the plane of the figure.

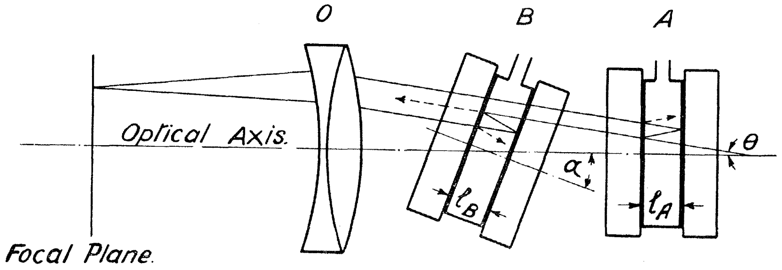

FIG. 1. Method of Fabry and Buisson as applied to refractivity measurements.

Monochromatic light from an extended source to the right of the figure is partially transmitted and partially internally reflected by the double étalon system in the manner indicated by the full lines and passes on towards the object lens of the telescope, which is focused for parallel light. The object lens produces, in its focal plane, a real image of the system of straight, parallel and equally spaced Brewster's fringes, which, in the circumstances represented in fig. 1, are perpendicular to the plane of the paper. In the same way as for the single Fabry-Perot étalon the effect of multiple reflexions within the two étalons gives rise to a system of fringes consisting of fine bright lines on a dark background, and this advantage of the method has been fully discussed by Fabry and others. It suffices to mention here that the brightest and sharpest fringes are obtained when the reflecting power of each étalon surface is 70 % or higher, and when the lengths l_A and l_B are nearly equal.

Reference has already been made to a special feature of the type of étalon used in this work, namely, that the space between the semi-reflecting surfaces is totally enclosed and airtight, and can be either evacuated or filled with air under known and controlled conditions. Suppose that, at first, both A and B are evacuated and that in this condition l_A is slightly greater than l_B. For our present purposes it is sufficient to consider only

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the simplest possible effects of internal reflexion and transmission by the two étalons. It will be seen in the upper part of fig. 1 how a ray, inclined at an angle θ to the optical axis, is divided into two parts at the second semi-reflecting surface of A, and that each part subsequently has imposed on it a relative retardation by being twice internally reflected, the one in A and the other in B. The amount of relative retardation is $2l_A \cos\theta$ in A and $2l_B \cos(\alpha-\theta)$ in B, where α represents the angle between the normal to the semi-reflecting surfaces of B and the optical axis of the telescope.

The condition for the formation of a bright fringe for all rays parallel to the direction θ is that N should be an integer in the equation

$$2l_A \cos\theta - 2l_B \cos(\alpha-\theta) = N\lambda, \qquad (2{\cdot}1)$$

where λ is the wave-length *in vacuo* of the monochromatic light used. The bright fringe formed under this condition is usually described as being of order of interference N.

The angle α in equation (2·1) controls the angular separation of the fringes. For, if the adjacent bright fringe of higher order $(N+1)$ is produced by rays parallel to the direction ϕ, then by analogy with equation (2·1) we have

$$2l_A \cos\phi - 2l_B \cos(\alpha-\phi) = (N+1)\,\lambda.$$

Subtracting equation (2·1) from this, we obtain

$$\lambda = 2l_A(\cos\phi - \cos\theta) - 2l_B[\cos(\alpha-\phi) - \cos(\alpha-\theta)].$$

Hence, since l_A is closely equal to l_B, and the angles ϕ, θ, $(\alpha-\phi)$ and $(\alpha-\theta)$ are small, and remembering that $\cos x = 1 - x^2/2$ when x is small, we have

$$(\theta-\phi) = \lambda/2l\alpha, \qquad (2{\cdot}2)$$

where $(\theta-\phi)$ is the angular separation of the two adjacent bright fringes, and $l = l_A$ or l_B. Thus, for a given λ and a given length of étalon, a convenient angular separation of the fringes can be obtained by adjusting the angle α between the normals to the two pairs of étalon surfaces.

If now air is slowly admitted to A, the Brewster's fringes will move across the focal plane of the telescope in a direction perpendicular to their lengths and keeping parallel to themselves. This displacement is due to the change in the optical length of A produced by the effect of the refractive index of the air. When A contains air of refractive index n, the relative retardation produced in A on the ray denoted by θ becomes $2nl_A \cos\theta$. If this value is substituted for $2l_A \cos\theta$ in equation (2·1), it will be seen that when n increases then θ must increase in order to maintain a constant N value, so that the fringe of order number N moves upward on the diagram (fig. 1) when air is being admitted to A.

It is of practical importance to consider the fringe displacement at a convenient reference point—e.g. that provided by the intersection of the optical axis of the telescope with its focal plane, this point of reference being generally denoted in telescopes by the point of intersection of horizontal and vertical cross-wires in the focal plane of the

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eyepiece. Since for this point θ is by definition equal to zero, then equation (2·1), for the condition when both étalons are evacuated, becomes

$$2l_A - 2l_B \cos\alpha = (N_1 + \epsilon_1)\,\lambda, \tag{2·3}$$

where N_1 is the integral and ϵ_1 the fractional part of the order of interference at the reference point corresponding to the difference represented by the left-hand side of equation (2·3). Similarly, if A contains air of refractive index n, and B remains evacuated, then

$$2nl_A - 2l_B \cos\alpha = (N_2 + \epsilon_2)\,\lambda, \tag{2·4}$$

where N_2 and ϵ_2 are integral and fractional parts, respectively, of the order of interference for this condition. From equations (2·3) and (2·4) we obtain

$$(n-1) = [(N_2 - N_1) + (\epsilon_2 - \epsilon_1)]\,\lambda/2\,l_A. \tag{2·5}$$

The expression $\lambda/2l_A$, outside the square brackets on the right-hand side of equation (2·5), is the inverse of the number of half wave-lengths *in vacuo* contained in l_A, and needs to be known to an accuracy of at least 1 part in 100,000, since the desired final accuracy of determination of $(n-1)$ is to be of the order of 1 part in 30,000. The method adopted for the determination of $\lambda/2l_A$ is precisely the same as that originally described by Fabry and Buisson, and which has since been used by the present authors for the optical measurement of lengths. The expressions $(N_2 - N_1)$ and $(\epsilon_2 - \epsilon_1)$, inside the square brackets, are respectively the integral and fractional parts of the total fringe displacement past the reference point during the admittance of air to A. If the rate of entry of air to the étalon is controllable by some such device as a needle valve the value of $(N_2 - N_1)$ may be obtained by counting the number of complete fringe widths (a fringe width being defined as the linear distance in the focal plane of the telescope between two adjacent bright fringes) which pass the reference point during the admittance of air. Other methods are available for deriving this number which either do not involve an actual count of the total number of fringes passing a cross-wire, or at most only require a small fraction of the total to be counted, and these will be described later.

The fractional part of the order of interference at the reference point, corresponding to each condition of the étalon A, is obtained by measuring, in the focal plane of the telescope, the linear distance of the reference point from the nearest fringe of lower order (which may be either above or below this point according to the disposition of the apparatus) and expressing it as a fraction of the fringe width. The sense in which the measurement is made is decided by determining in which direction the order is decreasing. Since the order is decreasing upwards in fig. 1 (cf. equation (2·1)) the measurement is made in this case with respect to the first fringe above the cross-wire, neglecting the effect of reversal that would occur in the image if it were viewed through the ocular of a micrometer eyepiece.

In practice the measurement of excess fractions is conveniently made by photographing at the same time the cross-wires and the real image of the fringes, and then

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determining the relative positions of fringes and reference point on the photographic negatives by means of a non-recording microphotometer. If the real image of the cross-wires and fringes is projected on to the slit of a spectrograph, all the data necessary for the calculation of the refractive indices for several radiations may be simultaneously photographed on a single plate. With such conditions of recording and measurement some slight sacrifice of the sharpness of the fringes, which is ideally possible by the method, must be made by reducing the reflecting power of each étalon surface to about 60 % or lower, in order that sufficient non-interfering light of all colours shall be directly transmitted by the two étalons to give a suitable impression of the position of the cross-wires upon the photographs.

It has been assumed in deriving equation (2·5) that both the mechanical lengths l_A and l_B remain unchanged during the experiment, so that the following corrections must be applied to the value of $(n-1)$ deduced from this equation:

(i) Correction for the change in dimensions of étalon A as a consequence of filling it with air, and

(ii) Correction for any relative changes in the dimensions of both étalons due to temperature variations.

The value of the correction due to (i) can be obtained by means of a separate experiment in which the distances between the semi-reflecting surfaces of A are optically compared before and after filling it with air by measuring the separations of these surfaces with reference to two fixed semi-transparent surfaces external to the étalon. The effect of (ii) may be reduced to almost negligible proportions by using invar étalons mounted inside a constant temperature enclosure.

A further temperature effect, due to the fact that the changes taking place in the air when it is being admitted to étalon A may not be isothermal, can be guarded against by reversing, in practice, the procedure which has been outlined above for convenience in explanation. The experiment is started with étalon A filled with air under the desired conditions of temperature, pressure and composition, the air having been admitted several hours previously and the air-filled étalon allowed to attain the temperature conditions of the surrounding enclosure. Étalon B being evacuated, the position of the fringes with respect to the reference point is observed; then the air is withdrawn from A as quickly as possible by connecting the étalon to a powerful vacuum pump, and the position of the fringes for the condition when both étalons are evacuated is observed. Although sudden expansion of air in the manner described is likely to be an adiabatic process, so little time is allowed for the comparatively massive wall of the étalon to be affected by the temperature changes in the air, which is being rapidly withdrawn from it, that an important source of error is thus eliminated.

It will already have become evident during this explanation of the method of Fabry and Buisson that the necessity for an extended source of light arises out of the requirement that the source must subtend a sufficient angle at the object lens of the telescope in order that an adequate area of the image of the Brewster's fringes should be available

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for observational purposes in its focal plane. This necessity leads to a difficulty when the étalons are of such lengths as were employed in this investigation (67 cm.). Reference to equation (2·2) shows that, for a given angular separation of the fringes, α decreases in the same proportion as l_A and l_B increase, and that when l_A and l_B are large α must be very small. But it is found in practice that when α is too small the image in the focal plane is confused by overlapping systems of Brewster's fringes. This confusion arises because the relatively inclined étalons are equivalent to a pair of semi-transparent mirrors inclined at a small angle, and produce, therefore, in the focal plane of the telescope a series of overlapping images of the source due to multiple reflexions. Each image exhibits under these conditions a different system of fringes.

The difficulty is overcome by restricting the source in the following manner. By means of a condensing lens an image of the source is projected on to a slit of variable width, arranged with its length parallel to the lengths of the fringes, e.g. perpendicular to the plane of the paper in fig. 1. The slit is situated at the principal focus of a collimating lens, and the collimated beam of light is directed along the optical axis of the telescope towards the double étalon system, where it is partially transmitted and internally reflected. The position of the slit is first adjusted until its principal image is arranged symmetrically about the intersection of the cross-wires in the focal plane of the telescope. Having already adjusted α to give the required angular separation of the fringes within the principal image, the slit width is then adjusted until the multiple images are just separated from one another. With this arrangement of the optical system and by using an object lens of about 45 cm. focal length in conjunction with the 67 cm. étalons, a linear fringe width of approximately 0·25 mm. is obtained in the focal plane for red light, and at least three fringe orders can be viewed within the limits of the width of the principal image of the slit without confusion due to overlapping systems. With such a fringe width in red light and a corresponding width of about 0·17 mm. in violet light an average accuracy of about 0·01 can generally be obtained in the determination of excess fractions by the employment of the microphotometric method of measuring the photographs.

3. Apparatus and experimental procedure

(*a*) *Optical apparatus*. The Wave-Length Comparator, which was used for these determinations of the refractive index of air, has already been fully described by the present authors (Sears and Barrell 1932). As the complex arrangement of optical apparatus, of which this comparator chiefly consists, had to be somewhat modified for the special purposes of refractometric work, a brief résumé is given here of the principal features of the original apparatus, with descriptions of the modifications and additions which have been made.

Fig. 2 is a diagram in plan view of the complete optical apparatus arranged for the measurement of refractive indices. The étalons, main telescope and optical com-

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parator, together with certain auxiliary apparatus such as mirrors, were mounted inside a thermally insulated, wooden enclosure on the slate top of a concrete pillar isolated from the surrounding building and enclosure. The sources of light, with their associated lens and mirror systems, and the spectrograph, were arranged in suitable positions outside the enclosure, double-glazed windows being provided where necessary in the walls of the enclosure to allow entry of light into it.

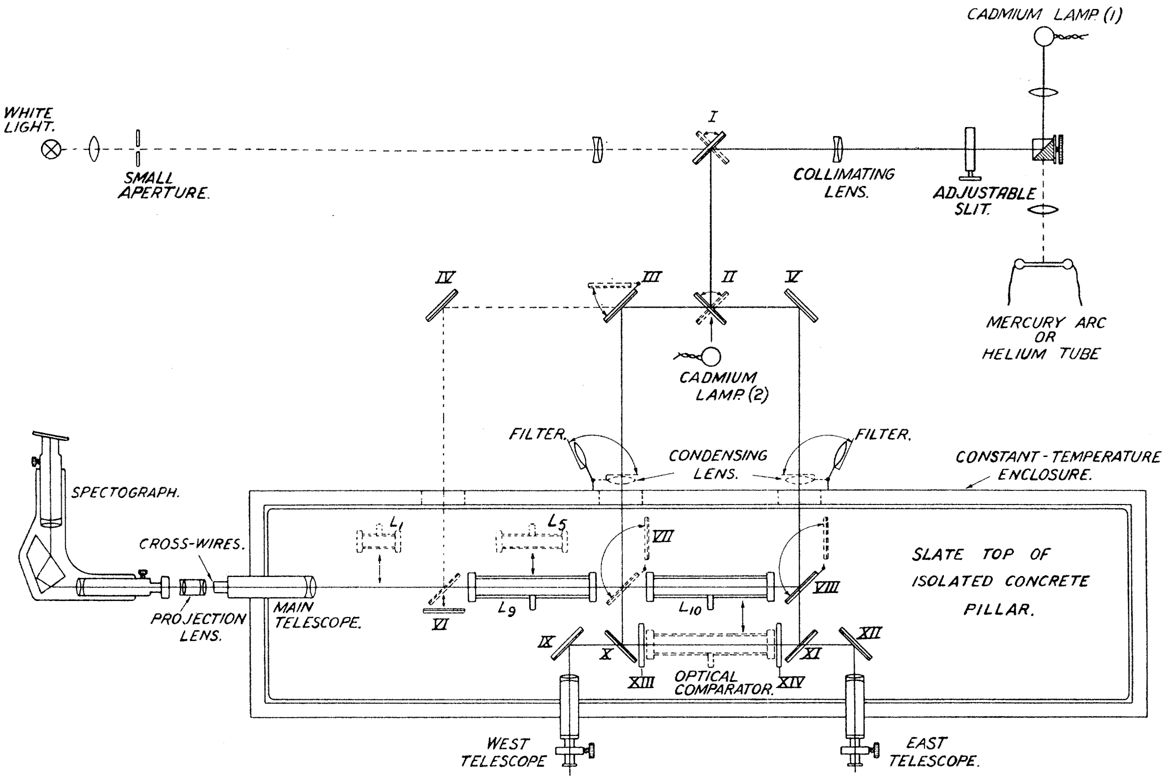

FIG. 2. Diagram of general arrangement of optical apparatus.

The two étalons of nominally equal lengths, used for the refractive index determinations, are denoted by the symbols L_9 and L_{10} on the diagram; they were the ninth and tenth members of a series of invar étalons of simply related lengths which have been constructed for various purposes. All étalons in this series have lengths which are simple fractions of the length of the longest étalon (approximately 1006·5 mm.) used in the absolute determinations of the fundamental units of length. As the arrangement of apparatus inside the enclosure did not conveniently permit of the use of two equal étalons of greater length than about two-thirds of a metre, L_9 and L_{10} were each constructed to be of nominal length about $\frac{2}{3} \times 1006{\cdot}5$ mm. or 671·0 mm. They were of the tubular invar type, with flat chromium-plated ends, which has been previously described by us (Sears and Barrell 1932). The optical reflecting surfaces of each étalon were formed by flat glass plates "wrung" to the ends of the tube, the plates being silvered only on those portions of their surfaces which covered the bore of the tube. As in former étalons, means were provided for elastically compressing the central portion

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of each tube in order to enable small adjustments of length and of the parallelism of the ends to be made.

Two other étalons of the series, namely, L_1 and L_5, indicated by dotted lines in fig. 2, were employed in determining the length of L_{10} by a method which has been previously described (Sears and Barrell 1932). Approximately, L_{10} was twice the length of L_5, and L_5 was four times the length of L_1. During determinations of the length of L_{10}, L_5 was substituted for L_9, L_1 was placed in a position in line with the main telescope, and the mirrors VI and VII were suitably adjusted to direct light into the étalons.

The supporting mechanism for the étalon L_{10} was specially designed to give accurately parallel displacements to the étalon placed upon it. This feature of the original apparatus fulfilled an important function in the present investigation, for it enabled the étalon to be moved from the position where its axis was coincident with the optical axis of the main telescope, to the position, shown in dotted line in fig. 2, between the two fixed mirrors XIII and XIV which constituted the reference base of the optical comparator, where the change of mechanical length of the air-filled étalon was observed during the withdrawal of the air.

No other adjustments for alignment of étalon L_{10} were provided, and therefore the central normal to the two parallel semi-reflecting surfaces of this étalon, when it was in the position shown in full line in fig. 2, was regarded as the datum line to which all other apparatus was adjusted. The main telescope was accordingly provided with alignment adjustments which allowed its optical axis to be brought into coincidence with this datum line by an auto-collimation process, during which étalon L_9 was removed from its support. The support for étalon L_9 was provided with separate adjustments for inclination and alignment.

The surfaces of the comparator mirrors XIII and XIV were semi-silvered, and were capable of adjustment into accurate optical parallelism with the reflecting surfaces of étalon L_{10} when the latter was disposed between them. The change in length of the air-filled étalon during exhaustion was then determined by measuring the change in the diameters of the Hamy fringes produced in reflected monochromatic light at each end of the comparator. In order to illuminate both ends of the comparator and at the same time to observe the interference phenomena, two semi-silvered mirrors X and XI, disposed in opposite senses at 45° to the axis of the comparator, and two small telescopes were provided, as depicted in fig. 2. The light partially reflected from the comparator mirrors XIII and XIV and from the reflecting surfaces of L_{10} was partially transmitted by the mirrors X and XI; it was then fully reflected by the mirrors IX and XII towards the telescopes, marked "West" and "East" respectively, where the interference rings were observed.

Full details of the method of calculating excess fractions from the observations on the optical comparator have been described previously (Sears and Barrell 1934). Briefly, measurements were made, with the aid of a micrometer eyepiece, of the linear diameters of five dark rings on a bright background, first at one telescope and then at

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the other. These measurements were then repeated in reverse order, and from the complete set of observations the mean value of the excess fraction corresponding to the centre of the interference ring system at each end of the comparator was calculated.

In its normal position, mirror VIII received light from the external optical system and directed it through the two étalons towards the main telescope, but when the comparator was in use this mirror was moved out of the beam which illuminated the right end of the comparator.

Passing now to optical apparatus outside the enclosure, it will be seen, in the upper part of fig. 2, how monochromatic light or white light can be directed into the enclosure through any one of the three windows by suitable arrangement of the fully silvered mirrors numbered I–V. White light was required for work involving the optical multiplication of lengths and was therefore only necessary for the determinations of length. Monochromatic radiations for the refractometric work was provided by three sources—cadmium lamp (1), mercury arc and helium tube—which were disposed in a vertical semicircle about a reflecting prism which was adjusted by rotation to reflect light from any one source at a time towards the horizontal slit. The function of this slit in controlling the linear dimension of the source in a vertical plane has already been described. Each source was provided with a condensing lens for projecting its image upon the slit. The slit was placed in the focal plane of the collimating lens (45 cm. focal length), and the collimated beam was then directed by mirrors I, II, V and VIII towards the étalons.

When the optical comparator was in use the cadmium lamp marked (2) was substituted for mirror II; light from this source was then directed by mirrors III and V towards the mirrors X and XI and thence into the optical comparator. With this arrangement simultaneous observation of the change in dimensions of L_{10} could be made, if desired, at both ends of the comparator. A combined condensing lens and red filter was placed in each of the two beams proceeding towards the optical comparator, the lens to give the required convergence in the rays for satisfactory production of the Hamy fringes, and the filter to isolate the red radiation of cadmium and thus provide monochromatic light for the comparator. These combinations were fixed to the outer wall of the enclosure and were turned to "off" positions when the comparator was not in use.

For the refractivity measurements the main telescope was normally used without its ocular, so that the real image of the Brewster's fringes, produced by the object lens in the plane of the cross-wires, could be farther projected, together with an image of the cross-wires themselves, by the compound projection lens upon the vertical slit of the spectrograph. The projection lens was arranged approximately in the position producing unit magnification. It is important to note that the reference point, denoted by the intersection of the vertical and horizontal wires in the focal plane of the object lens, was rigidly fixed by the telescope tube in relation to the object lens, so that no fortuitous linear displacement of the reference point with respect to the fringes was likely to occur during an experiment. To reduce as far as possible the transmission of

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vibration from the wall of the enclosure to the telescope tube, the tube passed through a hole thickly lined with felt. Similar arrangements were provided where the smaller telescopes, used with the optical comparator, emerged through the enclosure wall.

The spectrograph had collimator and camera lenses of about 50 cm. focal length and employed a glass prism of constant deviation type. On the photographic plate (Ilford Hypersensitive Panchromatic) the distance between the slit images for the cadmium red (6438 A) and mercury violet (4358 A) radiations was about 24 mm. Both the spectrograph and the projection lens were supported on the same table, standing on the floor of the room.

(*b*) *Auxiliary apparatus*. The auxiliary apparatus for preparing dry, CO_2-free air, and for the control and measurement of temperature and pressure, has already been described in connexion with the work on the Wave-Length Comparator (Sears and Barrell 1934). Certain modifications and additions have been made for the special purpose of this investigation, among which may be mentioned the incorporation of a cooling unit from a standard type of domestic refrigerator into the thermostat system associated with the enclosure, and the fitting of another vacuum pipe-line in order that the two étalons may be independently evacuated. A further addition, required for the experiments on moist air, provided means for introducing a known amount of water vapour to one of the étalons.

A diagram of the apparatus for controlling the composition of the samples of air on which refraction and dispersion measurements were to be made, and of the system of pipe-line connexions between the étalons and other auxiliary apparatus, is shown in fig. 3. Air from a garden, on the south side of the building in which the experiments were made, was drawn into the evacuated étalon L_{10} through the needle valve (1) at the rate of about 0·4 l./min. In its journey to the étalon the air passed first through a soda-lime tube, which abstracted the carbon dioxide, then through a calcium-chloride tube, for preliminary drying, and finally through a tube containing dehydrated silica gel, which abstracted the last traces of moisture.

Temperature measurements were made by means of two 50-ohm platinum resistance thermometers of standard design, the "bulbs" of the thermometers being placed as closely as possible to the étalons. One thermometer was associated with each étalon. The measurement of the "bulb" resistance was carried out by potentiometer comparison with a standard resistance of 50 ohms formed from two 100-ohm coils connected in parallel; the coils and thermometers were periodically calibrated against Laboratory standards.

Pressure measurements were made by connecting the air-filled étalon to the cistern of a specially designed barometer gauge, of the type generally known as the Kew Pattern instrument. The gauge was periodically standardized by reference to the Laboratory's Primary Standard (Sears and Clark 1933), and its accuracy of pressure measurement was approximately ±0·02 mm. throughout the range of pressure, from 100 to 800 mm., used in this investigation.

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It will be noticed in fig. 3 that a large reservoir, situated inside the étalon enclosure, is connected to the same pipe-line as étalon L_{10}, and this was normally filled at the same time as the étalon. The purpose of this reservoir was to increase the volume of air under

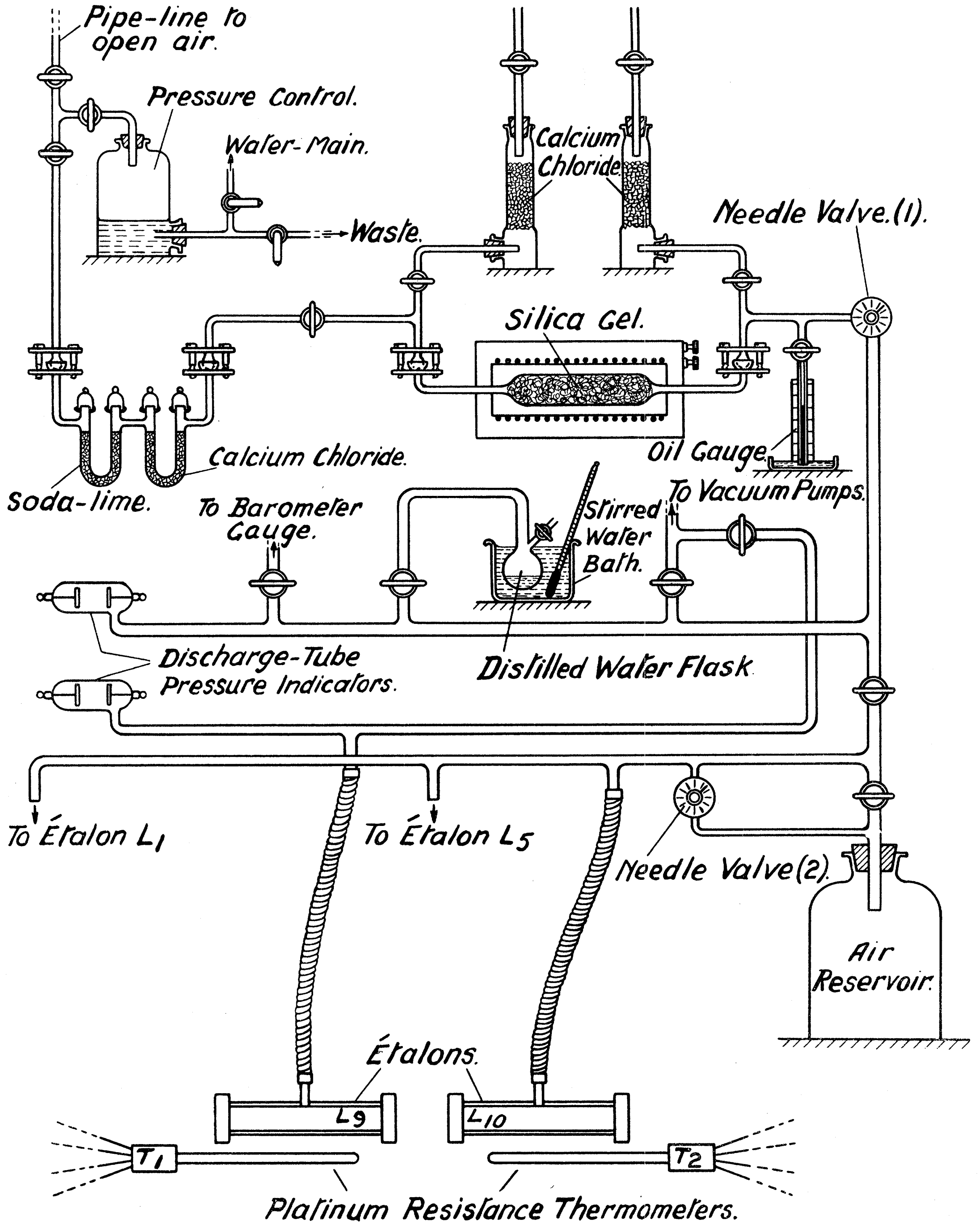

FIG. 3. Diagram of connexions to the auxiliary apparatus.

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precise temperature control, thus reducing the relative effect of the normal variation of ±0·1° C in room temperature upon the small volume of air in the pipe-line connecting the étalon with the externally mounted barometer gauge. Alternatively, the air reservoir could be disconnected from the étalon L_{10} and therefore remain evacuated when L_{10} was air-filled; under these circumstances air could be slowly withdrawn from the étalon through the needle valve (2) into the reservoir. This feature was employed in the preliminary counts of total fringe displacement due to a measured pressure change in L_{10}, and therefore the control knob of needle valve (2) was placed in a position near the spectrograph (see fig. 2), within easy reach of the observer's hand.

Both étalons were independently connected to the same vacuum pumps. One of these pumps was an oil-immersed rotary pump and was used for producing a fore-vacuum for the other, which was an electrically heated, oil vapour pump. A small discharge tube, with parallel plate electrodes, was connected to each étalon, and was used to indicate the degree of vacuum from the size of the Crooke's dark space produced when the tube was excited by a unidirectional discharge.

The arrangement of stopcocks and pipe-lines shown in the diagram enabled the following operations to be carried out:

(i) Maintenance of a vacuum in L_9 when L_{10} was air-filled and connected to the reservoir and the barometer gauge;

(ii) Production of a vacuum in L_{10} when it was disconnected from the reservoir and the barometer gauge, L_9 being temporarily disconnected from the pumps during this operation;

(iii) Maintenance of a vacuum in both L_9 and L_{10} simultaneously.

There was also provided in the pumping system an arrangement of stopcocks which allowed the oil-vapour pump to be temporarily isolated, while the backing pump produced a suitable low pressure in L_{10} for connexion to the oil-vapour pump.

Attention is drawn to the aspirator bottle labelled "Pressure Control" at the top left-hand corner of the diagram (fig. 3); this was used to force air into the étalon L_{10} and its connexions when it was desired to make experiments at pressures higher than atmospheric. It operated as a displacement system in which water from the mains, at a pressure of about 40 lb./sq. in. was allowed to enter at the bottom of the bottle, displacing air that had previously been drawn from outside the building when water was allowed to run out of the bottle. The action was controlled by the various stopcocks arranged in the aspirator connexions.

The distilled water flask which is shown, in fig. 3, connected through a stopcock to the same pipe-line as L_{10}, was only used during the experiments on moist air, which are described in a later section of this paper.

(*c*) *Sources of monochromatic radiations.* The cadmium source was an Osram discharge lamp of the hot-cathode type, which provided four brilliant radiations, red, blue-green, blue and blue-violet, in the visible spectrum; it was operated, in series with a ballast resistance, at a current of 1·25 amp. from the 220 V A.C. mains. The mercury source

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was a Cooper-Hewitt lamp with a 4 ft. arc length, operated from the 110 V D.C. mains at a current of about 3·5 amp., and the brilliant green and violet radiations were selected for use. Finally, the yellow and violet lines of helium from a Geissler tube, filled with helium at low pressure and excited by a transformer discharge at a potential difference of about 1500 V, made up the group of eight radiations; this source was employed in the broadside-on position and the current through it was limited by a water resistance to a value of about 10 mA.

In the fourth column of Table I are given the values adopted for the wave-lengths of the eight selected radiations, as referred to the normal air condition, viz. in dry air at 15° C and 760 mm. pressure, containing 0·03 % of CO_2. The fifth column gives the calculated values of the wave-lengths *in vacuo*, as derived from the values in normal air with the aid of the dispersion equation for normal air determined by Pérard (1934). These values *in vacuo* are employed later as approximate values for calculating a new dispersion equation for air. For the calculations concerned in the derivation of the length of one of the étalons in terms of wave-lengths of the various radiations given in Table I, the sixth column gives the ratios of the wave-length *in vacuo* of λ_1 to the wave-lengths *in vacuo* of the other seven radiations.

TABLE I. WAVE-LENGTHS OF THE SELECTED RADIATIONS

Source	Colour	Designation	λ_N (unit $= 1 \times 10^{-6}$ m.)	$\lambda_{\text{vac.}}$ (unit $= 1 \times 10^{-6}$ m.)	Ratios *in vacuo*
Cadmium	Red	λ_1	0·6438 4696*	0·6440 249	—
Helium	Yellow	λ_2	0·5875 623†	0·5877 252	1·095,792,6
Mercury	Green	λ_3	0·5460 743†	0·5462 260	1·179,044,7
Cadmium	Blue-green	λ_4	0·5085 8212‡	0·5087 239	1·265,961,7
Cadmium	Blue	λ_5	0·4799 9104‡	0·4801 252	1·341,368,7
Cadmium	Violet-blue	λ_6	0·4678 1493‡	0·4679 459	1·376,280,8
Helium	Violet	λ_7	0·4471 477†	0·4472 732	1·439,891,6
Mercury	Violet	λ_8	0·4358 325†	0·4359 550	1·477,273,9

* Internationally accepted value. † Pérard (1928). ‡ Sears and Barrell (1933).

(*d*) *Procedure in a determination of refractivity*. The procedure for one experiment on the refractivity of air consisted of two consecutive and similar sequences of operations, in the first of which the étalon L_{10} contained air, and in the second it was evacuated to a low pressure. Before the experiment commenced, L_{10} and its associated reservoir were first exhausted, and then air was allowed to enter at a suitable rate, controlled by the needle valve (1), until the required pressure, indicated by the barometer gauge, was obtained, when the influx was stopped. The air drawn into the apparatus was now left to acquire the temperature of the enclosure for a period of at least 2 hr., which had been found by previous experience to be amply sufficient for the purpose. If the subsequent observations of refractivity were to be made the next morning, the air was naturally left in the apparatus overnight, in order to allow experimental work to commence as early as possible on the following morning.

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Before commencing observations the étalon L_9 was exhausted and maintained at a low pressure of about 0·001 mm. Étalon L_{10} was then displaced to its position between the mirrors of the optical comparator where the distances between the reflecting surfaces of the mirror and étalon at the two ends were measured in terms of the red radiation of cadmium. After this L_{10} was moved back to the position where its axis was in line with the optical axis of the main telescope, and readings of the pressure in the étalon and of the temperatures of the two étalons were obtained before the photography of the fringes and reference point in the eight selected radiations was commenced.

The photography occupied a period of about 20 min., during which two exposures in the radiations from each source were made. The two exposures for each source were symmetrically disposed in time about the middle of this period so that mean values of the excess fractions for all radiations, as measured from the photographs, referred to this mean time.

The barometer gauge and thermometers were then read again and the étalon L_{10} was displaced into the optical comparator for a further measurement in terms of the cadmium red radiation.

This operation completed that part of the experimental procedure concerned with the air-filled condition of L_{10}; and by proper timing of the operations it was possible to obtain the mean temperatures of the individual étalons, the mean pressure in L_{10} and a set of photographs of fringe groups and cross-wires from which the mean values of the excess fractions for the eight radiations were measured, all means referring in time to the middle of the period of observation, provided that temperature and pressure changes were small or were assumed to be linear with time. Furthermore, a mean measure of the distance between the reflecting surfaces of L_{10} during its air-filled condition was known from the observations in the optical comparator.

Starting the second part of the experimental procedure with the étalon L_{10} still in its position between the comparator mirrors, the sequence of operations outlined above was repeated, but with L_{10} now exhausted to a low pressure of about 0·001 mm. so that no observations on the barometer gauge were taken. As a result of this second sequence it was possible to obtain the mean values of the temperatures of the two étalons together with photographs from which the mean values of the excess fractions were measured, all means referring in time to the middle of the period occupied in the second stage of the experiment. Also, the observations in the optical comparator gave a mean measure of the distance between the reflecting surfaces of étalon L_{10} when it was exhausted, from which, by comparison with the result of the similar observations in the air-filled condition, the lengthwise contraction of the étalon due to its exhaustion was derived.

4. DETERMINATIONS OF REFRACTIVITY FOR DRY, CO_2-FREE AIR

(*a*) *Sequence of observations.* The refractometric work was carried out in six main series of observations, each series at a different temperature, during a period extending from August 1935 to April 1937. Not the whole of this period was occupied in obser-

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vational work, for considerable intervals occurred between certain of the series to allow the microphotometric measurement of previously obtained records to be completed; and it was also found advantageous to fit in the observational work at different temperatures with the seasonal changes of temperature so that the difference of temperature between the étalon enclosure and its environs was reduced to a minimum. Moreover, the particular period mentioned happened to coincide with a phase of the present cycle of sunspot activity when this activity was increasing at its maximum rate, and therefore offered a very convenient opportunity for testing Tilton's suggestion regarding the relation between the refractivity of dry air and sunspot activity.

(*b*) *Values of the length of étalon* L_{10}. In view of the fact that invar, even when it has had stabilizing treatment, is subject to secular changes of length, the optical length of L_{10} was determined absolutely on three occasions during the period occupied by the measurements of refractivity, in order to obtain information concerning the magnitude of any such changes in length. The results of these three determinations, at different temperatures, are given in the third column of Table II.

TABLE II. VALUES OF THE LENGTH OF L_{10} IN TERMS OF $\frac{1}{2}\lambda_1$ (VAC.) AT VARIOUS DATES

Date of determination	Temperature (° C)	Observed length of L_{10}	Calculated length of L_{10}			
			At 20° C	At various temperatures (° C)		
August 1935	32·024	2,083,790·73	2,083,763·34	I	30·552	2,083,787
April 1936	20·194	2,083,766·52	2,083,766·08	II	25·214	2,083,778
				III	20·052	2,083,766
October 1936	20·131	2,083,767·82	2,083,767·52	IV	15·904	2,083,758
				V	12·053	2,083,749
April 1937	—	—	(2,083,769·3)	VI (*a*)	29·440	2,083,791
				VI (*b*)	29·479	2,083,791

A separate experiment at the beginning of the period had shown that the coefficient of thermal expansion of the optical distance between the reflecting surfaces of L_{10}, when evacuated, was $1{\cdot}093 \times 10^{-6}/1°$ C for the temperature range between 20 and 25° C.

Using this value of the coefficient of thermal expansion, the values of the length of L_{10} at 20° C, given in the fourth column of Table II, were calculated. It will be seen from these that secular changes of length were taking place, and that there is some evidence for the rate of change becoming less rapid during the latter part of the period of observation. As it was sufficiently accurate for our purpose to assume that the change was linear, during the whole period concerned, the length of L_{10} at 20° C for April 1937 was calculated by extrapolation from the total measured change of $+4{\cdot}18\,\lambda_1$ (vac.)/2 occurring during the first 14 months from August 1935 to October 1936, which corresponds to an average secular change of rather less than 1 part in 2×10^6 per annum in the length of the étalon.

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The values of the length of L_{10} shown in the seventh column of Table II were calculated from the 20° C values at the corresponding dates, and are the values finally used in the calculations of refractivity for the cadmium red radiation at the various mean temperatures shown in the preceding column. The corresponding values of the length of L_{10} in terms of the other seven radiations were derived from the values in terms of λ_1 (vac.)/2 by the use of the ratios given in Table I.

(*c*) *Values of the contraction correction.* Table III gives the observed values of the contraction of étalon L_{10} in terms of half wave-lengths of cadmium red radiation. Although each refractivity determination was accompanied by a contraction determination, it was finally considered preferable to use the smoothed values, shown under the columns headed "Calculated", rather than the individual values, for the purpose of correcting the refractivity measurements. These calculated values were obtained by deriving for each temperature series the weighted mean value of the correction corresponding to 100 mm., from which the values for other pressures were calculated by simple proportion, assuming the relation between contraction and pressure to be linear. The total observed fringe displacement in cadmium red radiation due to the evacuation of L_{10} was corrected for the consequent lengthwise contraction of L_{10} by subtracting the appropriate value of the calculated contraction given in Table III. Corrections in terms of the other radiations were obtained by using the known ratios between the wave-lengths of the radiations given in Table I.

TABLE III. OBSERVED AND CALCULATED VALUES OF THE CONTRACTION CORRECTIONS

(UNIT = $\frac{1}{2}\lambda_1$ VAC.)

Approx. pressure (mm.)	12·053° C		15·904° C		20·052° C		25·214° C		30·552° C	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100	0·036	0·087	0·055	0·088	0·132	0·094	0·111	0·091	0·087	0·087
200	0·155	0·174	0·186	0·177	0·197	0·187	0·178	0·180	0·167	0·173
300	0·266	0·261	0·247	0·266	0·285	0·281	0·275	0·270	0·227	0·260
400	0·347	0·348	0·363	0·354	0·346	0·375	0·376	0·360	0·350	0·345
500	0·455	0·434	0·453	0·442	0·449	0·469	0·453	0·450	0·405	0·431
600	0·567	0·521	0·540	0·531	0·559	0·562	0·556	0·541	0·514	0·517
700	0·609	0·608	0·630	0·620	0·632	0·656	0·604	0·631	0·651	0·605
800	0·693	0·695	0·712	0·708	0·774	0·750	0·691	0·721	0·709	0·691

(*d*) *Fringe displacement for a pressure change of* 100 *mm.* It is shown in equation (2·5) that, apart from small corrections due to dimensional changes of the two étalons, the refractivity of the air contained in one of the étalons, for a particular wave-length of radiation, is equal to the ratio of the total displacement of Brewster's fringes, which occurs when the étalon is exhausted, to the length of this étalon measured in terms of half wave-lengths *in vacuo* of the particular radiation. The spectrographic method of observation only recorded the relative positions of the fringes with respect to a point of reference before and after the air-filled étalon was exhausted, and therefore gave

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information upon the fractional part of the displacement only and none upon the integral part. The integral part could be determined either by calculation from previously obtained values of the refractivity of air, or by separate preliminary experiments in which direct counts were made of the fringe displacement past the reference point during the exhaustion of the air-filled étalon.

Owing to the variations existing between previously recorded values of the refractivity of air the integral part of the displacement could not be inferred from them with any greater certainty than ±1 part in 500, which would have led to possible ambiguities in fixing the total number of displaced fringes in the present investigation, where the expected displacement for 1 atm. approached 1000 fringes for the shortest wave-length used. Such a displacement would require a precision of ±1 part in 4000 in the assumed preliminary value of refractivity in order to avoid ambiguity in the calculated value of the displacement.

The method of direct counting of the fringes is also liable to uncertainties, unless performed automatically, since it must strictly be used for all the radiations, and this would have been difficult in the violet region where visual acuity is low.

The difficulty was overcome by combining the direct and indirect methods, using one method as a check upon the other, in a procedure whereby the fringe displacements in the eight radiations were determined for a limited change of pressure of about 100 mm. This procedure was based on a method described by Williams (1932), some variation of which had previously been used in other determinations of this kind. Starting with the étalon L_9 exhausted and with L_{10} containing air at a known temperature and at a measured pressure of, say, 700 mm., a photograph of the fringe groups superposed on the cross-wires in the eight radiations was taken. Then the pressure in L_{10} was reduced by an observed amount p_1 so that an average displacement of approximately 1 fringe was produced throughout the visible spectrum. In order to produce this displacement needle valve (2) was used in conjunction with the exhausted reservoir in the manner described in § 3 (*b*) of this paper, and the observer controlled the operation while observing the fringes in, say, mercury green light at the focal plane of the spectrograph with the aid of a reading lens. A second photograph was then taken. With the information available from the two photographs the integral and fractional parts of the displacement corresponding to the change of pressure p_1 were ascertained without ambiguity for the eight radiations.

The pressure in L_{10} was now reduced again by an additional amount $2p_1$ so that the total pressure change from the beginning (p_2) was about $3p_1$, and a third photograph was taken. By comparing the first and third photographs the fractional part of the total fringe displacement was ascertained, and the integral part was derived from the knowledge that the total displacement was very closely equal to p_2/p_1 times the displacement observed during the first pressure reduction, the result of this calculation being checked also by observing the number of fringes displaced in mercury green light while the second pressure reduction was taking place.

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This process was repeated until the pressure in L_{10} had been reduced to about 600 mm., corresponding to a total reduction of about 100 mm. As the total reduction of pressure at any stage was made approximately three times the total reduction at the preceding stage, the complete number of stages of reduction required was five, thus involving six different conditions of pressure in L_{10} and therefore six photographs. From these it was finally possible to obtain the integral and fractional parts of the fringe displacements, for the eight radiations, corresponding to a known change of pressure of about 100 mm., from which the corresponding values of refractivity at the temperature of the experiment were calculated. As a check on these the calculated values of refractivity of air under the same temperature and for a pressure of 100 mm. were obtained from the dispersion equation published by Pérard (1934), whose result for (n_D-1) was known to be closely the same as the mean value of all observers since 1857.

Separate experiments of this character were made at the maximum, mean and minimum temperatures of the range investigated.

It will be seen in the succeeding section of this paper that the observations of refractivity at any particular temperature were spaced at every 100 mm. pressure, so that a knowledge of the total fringe displacement corresponding to a pressure change in L_{10} from 700 to 600 mm. provided sufficient information for the calculations of refractivity at each stage of pressure from 100 mm. upwards. The only assumption made in this method was that the change of refractivity with pressure was approximately linear at constant temperature, and as it is later shown that the departure from linearity is less than 1 part in 10^6, no uncertainties could arise in the derivation of integral parts of total fringe displacements by the method which has been described.

(*e*) *Definitive measurements.* Of the six series of observations of refractivity made upon dry, CO_2-free air at the different mean temperatures shown in the sixth column of Table II, the first five each consisted of eight experiments at different pressures from 100 mm., by steps of 100 mm., to 800 mm. of mercury. The first part of the sixth series, made in April 1937, consisted of five experiments on dry, CO_2-free air, each at a pressure of about 760 mm. and at a mean temperature near that of the first series. By comparing the results of series I and VI (*a*) it was possible to impose a critical test upon Tilton's suggested relationship between refractivity and sunspot activity. The second part of the sixth series consisted of four experiments with moist air at pressures of about 760 mm., which will be described in a later section of this paper.

The experimental work in each of the first five series was precisely similar and generally occupied a period of from 4 to 5 days. Usually two experiments on air at different pressures were made in one day, one in the morning and the other in the afternoon, and a normal daily sequence in a single series was:

1st day, experiments at 700 and 500 mm.,
2nd day, experiments at 300 and 100 mm.,
3rd day, experiments at 200 and 400 mm.,
4th day, experiments at 600 and 800 mm.

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As a result, therefore, of five such series as this, forty independent values of the refractivity were obtained for each of the eight selected radiations in the visible spectrum. The method of calculating refractivity has already been explained, and in Table VIII (pp. 34–37) are given the 320 observed values of refractivity together with the corresponding temperatures and pressures.

5. General interpolation equations for dry, CO_2-free air

(*a*) *Preliminary calculation.* For the preliminary calculation, the results were fitted to the following general interpolation equation:

$$(n_{t,p}-1) = \left[A+\frac{B}{\lambda^2}+\frac{C}{\lambda^4}\right]\frac{p(1+\beta p)}{1+\alpha t}. \tag{5·1}$$

In this equation, $(n_{t,p}-1)$ represents the refractivity, for a wave-length λ, of dry, CO_2-free air at a temperature t° C in the International Scale and at a pressure corresponding to p mm. of mercury at 0° C ($g = 980·665$ cm./sec./sec.); A, B and C are the three constants of a Cauchy type dispersion formula which was found to be amply sufficient to represent the dispersion of air for the visible spectrum within the limits of the experimental accuracy achieved, and λ is the wave-length *in vacuo*, expressed in microns. α is the temperature coefficient of refractivity and β is Mascart's constant (see equation (1·4)), the magnitude of which is a measure of the departure from linearity of the refractivity-pressure relationship at constant temperature.

In the method adopted for reducing the observations to the form of (5·1), the group of eight results obtained for one radiation at any one temperature was first treated independently for the purpose of calculating a value of β. Thus, for each radiation, five values of β were derived, one from each series of results at eight different pressures and at an approximately constant temperature.

As the eight results in any one series referred to slightly differing temperatures (see Table VIII, p. 34) the initial stage was the reduction of each result to the mean temperature of the corresponding series. For this purpose the approximate value $\alpha = 0·00367$ per 1° C was accepted as a sufficiently accurate value of the temperature coefficient of refractivity for dealing with the small temperature differences involved. Confining attention for the moment to the refractivity for a given radiation and at a given pressure, let $(n'-1)$ represent the measured refractivity at temperature t' and let $(n-1)$ represent the corrected value at the mean temperature t of a series. Then, by equation (5·1),

$$(n-1) = (n'-1)\,(1+\alpha t')/(1+\alpha t).$$

Having corrected the five series of results for each radiation by this means, a value of β was calculated from a least squares solution of each series of eight equations corresponding to the different pressures. For a given radiation and at constant temperature, equation (5·1) reduces to the same form as Mascart's relation (see equation (1·4)):

$$(n_p-1) = kp(1+\beta p) = kp+k\beta p^2, \tag{5·2}$$

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where k and β are constants. One value of β was calculated from each series of eight equations of this type by the usual least squares method, so that, in all, forty values of β were obtained from the observations made with eight radiations at five different mean temperatures.

The least squares calculations are considerably simplified by previously correcting the results at different pressures to the corresponding values at the neighbouring exact pressures of 100, 200 mm., etc. Since the actual pressures do not, in any case, depart from the exact series by an amount exceeding 1 % of the value of the pressure, such correction can be performed with sufficient accuracy by a simple proportional calculation, for it is shown later that the value of β is exceedingly small and therefore the refractivity-pressure relation may be treated as linear for this purpose. With the adjusted values so obtained the formation of squares and higher powers of the values of pressure, together with other arithmetical products necessary for the least squares solution, are rendered much less tedious.

Table IV displays the forty values of $\beta \times 10^6$ thus determined, and it will be seen that, despite the comparatively large variations among the individual values, the mean values both by temperature and by wave-length exhibit reasonable constancy. From this evidence it was considered that the grand mean value of $\beta = 0{\cdot}73 \times 10^{-6}$ might be accepted as applicable to the whole range of temperature investigated and to the whole visible spectrum.

TABLE IV. VALUES OF $\beta \times 10^6$

Radiation	12·053° C	15·904° C	20·052° C	25·214° C	30·552° C	Mean
λ_1	0·81	0·89	0·47	0·84	0·57	0·72
λ_2	0·60	1·19	0·38	0·73	1·10	0·80
λ_3	0·59	0·90	0·52	0·72	1·02	0·75
λ_4	0·43	0·69	0·86	0·65	0·57	0·64
λ_5	0·51	0·71	0·64	0·71	0·34	0·58
λ_6	0·77	0·84	0·60	0·94	0·34	0·70
λ_7	0·78	0·83	0·65	0·77	1·20	0·85
λ_8	0·63	1·06	0·72	0·82	0·86	0·82
Mean	0·64	0·89	0·60	0·77	0·75	0·73

Each independent value of β in Table IV is associated with a corresponding value of k, and, having fixed on a definite value of β, adjusted values of k were next derived from the original series of equations in the following manner. Simple addition of each series of eight such equations as (5·2) produced five equations for each radiation of the form

$$\Sigma[(n_p-1)] = k\{\Sigma[p]+\beta\Sigma[p^2]\}.$$

In each of these equations the value $\beta = 0{\cdot}73 \times 10^{-6}$ was substituted and five values of k, corresponding to the five different mean temperatures, were calculated for each radiation.

A value of α for each radiation was now derived from the five values of k thus obtained. If the five mean temperatures are denoted by $t_1, t_2, \ldots$ and t_5 and the corresponding

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values of k for a particular radiation are denoted by $k_1, k_2, \ldots$ and k_5, then, since by equations (5·1) and (5·2)

$$k = (n_{t,p}-1)/p(1+\beta p) = [A+B\lambda^{-2}+C\lambda^{-4}]/(1+\alpha t),$$

therefore
$$k_1(1+\alpha t_1) = k_2(1+\alpha t_2) = \ldots = k_5(1+\alpha t_5) = K, \tag{5·3}$$

where K is a constant for a particular radiation and equal to $[A+B\lambda^{-2}+C\lambda^{-4}]$. A least squares solution of each series of five equations similar to (5·3) gave an independent value of α for each radiation.

Table V gives the eight values of α thus calculated, each value being derived from all the results obtained in one radiation. It will be noticed that there is no definite trend of the values with wave-length, and the mean value $\alpha = 0{\cdot}003674$ per 1° C was therefore adopted for the whole visible spectrum.

TABLE V. VALUES OF α AND K

($\beta = 0{\cdot}73 \times 10^{-6}$ per 1 mm.)

		$K \times 10^6$		
Radiation	α	Adjusted values	Calculated values	Adjusted − calculated
λ_1	0·003,665	0·383,431	0·383,425	+0·000,006
λ_2	0·003,682	0·384,498	0·384,507	−0·000,009
λ_3	0·003,684	0·385,536	0·385,538	−0·000,002
λ_4	0·003,677	0·386,706	0·386,701	+0·000,005
λ_5	0·003,667	0·387,793	0·387,786	+0·000,007
λ_6	0·003,671	0·388,311	0·388,312	−0·000,001
λ_7	0·003,671	0·389,302	0·389,311	−0·000,009
λ_8	0·003,675	0·389,927	0·389,922	+0·000,005
Mean	0·003,674			$\pm 0{\cdot}000{,}005_5$

An adjusted value of K was now derived for each radiation by adding each group of five equations of type (5·3), and then substituting the mean value of α in each of the eight equations of the following form so produced: $K = \{\Sigma[k] + \alpha . \Sigma[kt]\}/5$. From these equations the "adjusted" values of K given in column 3 of Table V were found.

The dispersion constants A, B and C were now determined by a least squares solution of eight equations of the following form:

$$K = A + B\lambda^{-2} + C\lambda^{-4}. \tag{5·4}$$

In these the values of wave-lengths *in vacuo* were used, expressed in microns as quoted in Table I. The values of the dispersion constants were found to be

$$A = 0{\cdot}378{,}153 \times 10^{-6}, \quad B = 2{\cdot}1442 \times 10^{-9} \quad \text{and} \quad C = 17{\cdot}59 \times 10^{-12}.$$

Using these values of the dispersion constants the values of K were recalculated from equation (5·4), and these values are shown in the fourth column of Table V. Comparing them with the adjusted values, which were derived directly from the obser-

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vations of refractivity after suitable values had been assigned to the constants α and β, it will be seen that the adjusted values fit the calculated dispersion curve to an average accuracy of ± 1 part in 70,000 of their magnitude.

The complete interpolation equation obtained from this preliminary calculation for dry, CO_2-free air, is

$$(n_{t,p}-1)\,10^6 = \left[0{\cdot}378{,}153+\frac{0{\cdot}002{,}144{,}2}{\lambda^2}+\frac{0{\cdot}000{,}017{,}59}{\lambda^4}\right]\frac{p(1+0{\cdot}73p\times 10^{-6})}{1+0{\cdot}003674\,t}. \qquad (5{\cdot}5)$$

A more conventional form of equation (5·5) is that in which the refractivity is referred to dry, CO_2-free air at 760 mm. and at either 0 or 20° C. In the present instance, since the mean temperature of the range investigated was about 20° C, it is more suitable to refer it to the latter temperature condition.

Since $p(1+\beta p)/(1+\alpha t) = 708{\cdot}371$ when $p = 760$ mm. and $t = 20°$ C, therefore

$$(n_{20,760}-1)\,10^6 = 267{\cdot}873+1{\cdot}5189\,\lambda^{-2}+0{\cdot}01246\,\lambda^{-4}. \qquad (5{\cdot}6)$$

At a temperature $t°$ C and pressure p mm.,

$$(n_{t,p}-1) = (n_{20,760}-1)\,p(1+\beta p)\,(1+20\alpha)/760(1+760\beta)\,(1+\alpha t), \qquad (5{\cdot}7)$$

where $\alpha = 0{\cdot}003674$ and $\beta = 0{\cdot}73\times 10^{-6}$.

(*b*) *Calculation of a new general interpolation equation.* It was felt to be desirable to analyse the relationship between the results obtained from the refractivity measurements and the corresponding variations in the density of the air. In doing so it appeared that the formulae obtained from the preliminary calculation given in the preceding section, although representing the results with sufficient accuracy, were not, theoretically, in the most appropriate form. A recalculation was therefore made, of an alternative form of interpolation equation, derived partly from theoretical and partly from empirical considerations based on D. Berthelot's representation of the characteristic behaviour of gases at low pressures, and on the Lorenz-Lorentz expression for the relation between the refractive index and density of transparent media. The new equation takes the form

$$(n_{t,p}-1) = \left[A+\frac{B}{\lambda^2}+\frac{C}{\lambda^4}\right]\frac{p(1+\beta_t p)}{1+\alpha t}. \qquad (5{\cdot}8)$$

The reasons underlying the choice of this particular form of equation will be discussed in more detail in a later section. Its distinguishing features are first, that $\alpha = 0{\cdot}003661$, corresponding to the theoretical expansion constant for a perfect gas, and second, that β_t is not constant but varies with temperature. Within the limits of temperature from 12 to 31° C covered by the present investigation we find that the relation between β_t and temperature may be represented with sufficient accuracy by the simple linear equation

$$\beta_t = a-bt, \qquad (5{\cdot}9)$$

where a and b are constants for the visible spectrum.

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As in the preliminary reduction of the results, attention was first confined to the groups of forty results obtained for particular radiations in calculating the values of β_t. Thus, for a given radiation, equation (5·8) becomes

$$(n_{t,p}-1)=\frac{Kp\{1+(a-bt)\,p\}}{1+\alpha t},\tag{5·10}$$

where $K=A+B\lambda^{-2}+C\lambda^{-4}$.*

No preliminary adjustment of the results to mean temperatures and exact pressures was made, as in the preliminary calculation, and a least squares method was directly applied to obtain the values of a and b from the forty observations for a single radiation. Equation (5·10) may be put into the following form:

$$r=fX+gY-hZ,\tag{5·11}$$

where $r=(n_{t,p}-1)$, $f=p/(1+\alpha t)$, $g=p^2/(1+\alpha t)$, $h=p^2t/(1+\alpha t)$, $X=K$, $Y=Ka$ and $Z=Kb$. From the forty equations of type (5·11) the values of X, Y and Z for each radiation were calculated.

The values of a and b derived for each radiation from the values of X, Y and Z thus obtained are given in Table VI. It will be seen that there is no definite trend of the values of a and b with wave-length, and the mean values were therefore assumed to be applicable to the whole visible spectrum. As a matter of interest and for purposes of comparison with the results given in Table IV, the five values of β_t corresponding to each radiation have been calculated and are shown in the same row as the values of a and b from which they were calculated. The grand mean value of β_t regardless of temperature is $0·72\times10^{-6}$ and is identical, within the possible error due to the rounding off of the last significant figures, with the value of $0·73\times10^{-6}$ derived from the preliminary calculation.

TABLE VI. VALUES OF $a\times10^6$, $b\times10^6$ AND $\beta_t\times10^6$

			$\beta_t\times10^6=a-bt$					
Radiation	$a\times10^6$	$b\times10^6$	12·053° C.	15·904° C.	20·052° C.	25·214° C.	30·552° C.	Mean 20·755° C.
λ_1	0·877	0·0078	0·78	0·75	0·72	0·68	0·64	0·71
λ_2	1·269	0·0234	0·99	0·90	0·80	0·68	0·55	0·78
λ_3	1·300	0·0270	0·98	0·87	0·76	0·62	0·48	0·74
λ_4	1·025	0·0191	0·80	0·72	0·64	0·54	0·44	0·63
λ_5	0·777	0·0097	0·66	0·62	0·58	0·53	0·48	0·57
λ_6	0·982	0·0136	0·82	0·77	0·71	0·64	0·57	0·70
λ_7	1·019	0·0089	0·91	0·88	0·84	0·79	0·75	0·83
λ_8	1·141	0·0162	0·95	0·88	0·82	0·73	0·65	0·81
Mean	1·049	0·0157	0·86	0·80	0·73	0·65	0·57	0·72

Having decided that fixed values of $a=1·049\times10^{-6}$ and $b=0·0157\times10^{-6}$ could be assigned in the interpolation equation, it was then possible to calculate the corresponding adjusted values of K from the original equations. By adding each group of

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* The constants A, B and C are, of course, not identical with those of equation (5·1).

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forty equations of type (5·11), eight equations of the following form were obtained, one for each radiation:

$$\Sigma[r] = K\{\Sigma[f] + a\Sigma[g] - b\Sigma[h]\}.$$

From these, eight adjusted values of K were calculated. These values are given in Table VII and from them the three dispersion constants were calculated by a least squares solution of eight equations similar to equation (5·4), in the manner which has already been described. The values of the dispersion constants thus determined were

$$A = 0{\cdot}378{,}065{,}4 \times 10^{-6}, \quad B = 2{\cdot}140{,}98 \times 10^{-9} \quad \text{and} \quad C = 17{\cdot}936 \times 10^{-12}.$$

The calculated values of K, derived from the dispersion equation with these constants, are given in Table VII for purposes of comparison with the adjusted values, which were derived from the observed results for refractivity after the relation between β_t and temperature had been fixed. It will be seen that the agreement between adjusted and calculated values of K is little different from that shown in Table V and on the average is within the limits of ±1 part in 70,000 of the magnitude of K.

Table VII. Values of $K \times 10^6$

($\alpha = 0{\cdot}003661$ per 1° C.; $\beta_t = (1{\cdot}049 - 0{\cdot}0157t)\ 10^{-6}$ per 1 mm.)

	$K \times 10^6$		
Radiation	Adjusted	Calculated	Adjusted − calculated
λ_1	0·383,337	0·383,332	+0·000,005
λ_2	0·384,404	0·384,414	−0·000,010
λ_3	0·385,442	0·385,443	−0·000,001
λ_4	0·386,611	0·386,606	+0·000,005
λ_5	0·387,697	0·387,690	+0·000,007
λ_6	0·388,215	0·388,217	−0·000,002
λ_7	0·389,206	0·389,216	−0·000,010
λ_8	0·389,832	0·389,827	+0·000,005
Mean		$(K_m \times 10^6 = 0{\cdot}3868)$	$\pm 0{\cdot}000{,}005_6$

The final form of the new interpolation equation is, therefore,

$$(n_{t,p} - 1)\,10^6 = \left[0{\cdot}378{,}065 + \frac{0{\cdot}002{,}141{,}0}{\lambda^2} + \frac{0{\cdot}000{,}017{,}94}{\lambda^4}\right] \times \frac{p\{1 + (1{\cdot}049 - 0{\cdot}0157t)\,p\,.\,10^{-6}\}}{1 + 0{\cdot}003661t}. \qquad (5{\cdot}12)$$

(*c*) *Comparison of observed and calculated results.* The whole of the 320 observed values are shown, with the temperatures and pressures of observation, in Table VIII, together with the corresponding values computed from the two alternative interpolation formulae and the differences between the observed and calculated values.

The calculated values of refractivity derived from equation (5·5) are given in the columns headed "Calculated I", and in succeeding columns the differences from the

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observed values are given in units of $0{\cdot}01\times10^{-6}$ under the headings "$(O-C)$ I". In order to economize space, only the last three significant figures of calculated values are given in the table.

The calculated values of refractivity derived from equation (5·12) are given under the heading "Calculated II", and the difference between the observed and calculated values are given under the heading "$(O-C)$ II".

In comparing the results of the calculation of refractivities from the two interpolation equations it will be seen that in no case does the difference between the two corresponding calculated values exceed $0{\cdot}01\times10^{-6}$, and on the average they may be regarded as giving identical values. The average residual for the two equations is $\pm0{\cdot}01_6\times10^{-6}$ for I and $\pm0{\cdot}01_7\times10^{-6}$ for II and the maximum residuals are $\pm0{\cdot}07\times10^{-6}$ in both cases. On the basis of the well-known equation for calculating the probable error of a single observation from the mean of a group of observations, namely, p.e. $=\pm0{\cdot}6745\sqrt{\{\Sigma[e^2]/(s-1)\}}$, where $\Sigma[e^2]$ = sum of squares of residuals, and s = number of observations, the probable magnitude of the deviation of a single observed value of refractivity in Table VIII from the dispersion curves represented by equations (5·5) and (5·12) is $\pm0{\cdot}014_6\times10^{-6}$ in each case, the calculated deviation being actually slightly the smaller from the new equation (5·12). Thus, either interpolation equation may be used to represent the results with equal accuracy, but on theoretical grounds, which will be referred to in more detail in the next section of this paper, we consider that equation (5·12) is to be preferred.

6. Relationship between refractive index, temperature and pressure of air

(*a*) *Relations between refractive index and density in the visible spectrum.* The Gladstone and Dale expression (1·2) and the Cauchy interpolation equation (1·6) are both special cases, the former for a given radiation and the latter for a given gas at constant density, of a more general empirical interpolation equation, which for a gas such as air and in the visible spectrum may take the following form:

$$(n-1) = [a_1+b_1\lambda^{-2}+c_1\lambda^{-4}]\,d, \tag{6·1}$$

where d is the density of the gas.

In a similar manner the Newton-Laplace expression (1·1) and the Sellmeier dispersion equation (1·7) are special cases of the more general formula

$$(n^2-1) = d\,.\,\Sigma_m[D_m/(\nu_m^2-\nu^2)],$$

in which the values of D_m are constants corresponding to the various frequencies ν_m of lines in the absorption spectrum of the gas concerned. In the case of a medium such as air, for which the value of n is greater than unity, one or more of these lines must lie in the ultra-violet region, and it is found in practice that even if there are any

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TABLE VIII. OBSERVED AND CALCULATED VALUES OF REFRACTIVITY OF DRY, CO_2-FREE AIR

		λ_1					λ_2				
		$(n-1)\,10^6$					$(n-1)\,10^6$				
Temperature (° C)	Pressure (mm.)	Observed (O)	Calculated		$O-C$		Observed (O)	Calculated		$O-C$	
			I	II	I	II		I	II	I	II
12·074	100·307	36·82	6·83	6·83	−1	−1	36·93	6·93	6·93	0	0
12·058	200·139	73·46	3·49	3·49	−3	−3	73·70	3·70	3·70	0	0
12·073	300·488	110·32	0·34	0·34	−2	−2	110·64	0·66	0·65	−2	−1
12·063	400·269	146·98	7·00	7·00	−2	−2	147·42	7·42	7·41	0	+1
12·035	500·250	183·73	3·75	3·75	−2	−2	184·28	4·27	4·27	+1	+1
12·055	600·380	220·54	0·53	0·53	+1	+1	221·14	1·16	1·15	−2	−1
12·008	700·280	257·29	7·29	7·29	0	0	258·02	8·02	8·02	0	0
12·060	800·634	294·07	4·13	4·13	−6	−6	294·94	4·96	4·96	−2	−2
15·910	100·058	36·25	6·25	6·25	0	0	36·35	6·35	6·35	0	0
15·896	200·158	72·50	2·52	2·52	−2	−2	72·72	2·73	2·72	−1	0
15·907	300·203	108·79	8·77	8·77	+2	+2	109·07	9·08	9·08	−1	−1
15·902	400·406	145·13	5·09	5·09	+4	+4	145·51	5·50	5·50	+1	+1
15·901	500·294	181·29	1·30	1·30	−1	−1	181·78	1·82	1·81	−4	−3
15·906	600·176	217·57	7·51	7·51	+6	+6	218·14	8·13	8·12	+1	+2
15·897	700·472	253·93	3·89	3·89	+4	+4	254·63	4·60	4·60	+3	+3
15·914	800·190	290·07	0·03	0·04	+4	+3	290·89	0·85	0·86	+4	+3
20·053	100·022	35·71	5·72	5·72	−1	−1	35·82	5·82	5·82	0	0
20·059	200·074	71·48	1·46	1·46	+2	+2	71·68	1·66	1·66	+2	+2
20·027	300·112	107·19	7·21	7·21	−2	−2	107·52	7·51	7·51	+1	+1
20·046	400·145	142·96	2·94	2·94	+2	+2	143·35	3·35	3·35	0	0
20·080	500·228	178·69	8·69	8·69	0	0	179·21	9·19	9·19	+2	+2
20·071	600·260	214·45	4·44	4·44	+1	+1	215·07	5·05	5·05	+2	+2
20·073	700·326	250·21	0·21	0·21	0	0	250·91	0·91	0·91	0	0
20·008	800·257	285·97	5·99	6·00	−2	−3	286·79	6·80	6·80	−1	−1
25·191	100·460	35·23	5·26	5·26	−3	−3	35·34	5·36	5·36	−2	−2
25·204	200·242	70·26	0·28	0·28	−2	−2	70·49	0·48	0·48	+1	+1
25·175	300·328	105·44	5·43	5·43	+1	+1	105·71	5·73	5·73	−2	−2
25·215	400·182	140·47	0·47	0·48	0	−1	140·87	0·87	0·87	0	0
25·240	500·224	175·58	5·59	5·59	−1	−1	176·07	6·08	6·09	−1	−2
25·230	600·074	210·65	0·66	0·66	−1	−1	211·26	1·25	1·25	+1	+1
25·226	700·117	245·82	5·80	5·80	+2	+2	246·49	6·49	6·49	0	0
25·231	800·092	280·90	0·91	0·91	−1	−1	281·69	1·71	1·71	−2	−2
30·534	100·964	34·84	4·81	4·81	+3	+3	34·88	4·91	4·91	−3	−3
30·540	200·690	69·21	9·20	9·20	+1	+1	69·38	9·39	9·40	−1	−2
30·547	301·763	104·02	4·05	4·06	−3	−4	104·31	4·35	4·35	−4	−4
30·544	400·182	138·05	8·00	8·01	+5	+4	138·38	8·39	8·40	−1	−2
30·582	500·395	172·53	2·55	2·55	−2	−2	172·98	3·03	3·04	−5	−6
30·535	599·731	206·92	6·85	6·85	+7	+7	207·44	7·43	7·43	+1	+1
30·615	702·230	242·18	2·15	2·15	+3	+3	242·84	2·84	2·84	0	0
30·521	800·703	276·22	6·22	6·21	0	+1	276·96	7·00	6·99	−4	−3

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TABLE VIII (*continued*)

		λ_3					λ_4				
		$(n-1)\,10^6$					$(n-1)\,10^6$				
Temperature (° C)	Pressure (mm.)	Observed (O)	Calculated		$O-C$		Observed (O)	Calculated		$O-C$	
			I	II	I	II		I	II	I	II
12·074	100·307	37·01	7·03	7·03	−2	−2	37·13	7·14	7·14	−1	−1
12·058	200·139	73·90	3·90	3·89	0	+1	74·13	4·12	4·12	+1	+1
12·073	300·488	110·94	0·95	0·95	−1	−1	111·28	1·29	1·28	−1	0
12·063	400·269	147·83	7·81	7·81	+2	+2	148·26	8·26	8·25	0	+1
12·035	500·250	184·79	4·77	4·76	+2	+3	185·34	5·32	5·32	+2	+2
12·055	600·380	221·76	1·75	1·75	+1	+1	222·42	2·42	2·41	0	+1
12·008	700·280	258·73	8·71	8·71	+2	+2	259·47	9·49	9·49	−2	−2
12·060	800·634	295·73	5·75	5·75	−2	−2	296·61	6·64	6·65	−3	−4
15·910	100·058	36·43	6·45	6·45	−2	−2	36·57	6·56	6·56	+1	+1
15·896	200·158	72·93	2·92	2·92	+1	+1	73·15	3·14	3·14	+1	+1
15·907	300·203	109·38	9·37	9·37	+1	+1	109·71	9·70	9·70	+1	+1
15·902	400·406	145·90	5·89	5·89	+1	+1	146·38	6·33	6·33	+5	+5
15·901	500·294	182·30	2·30	2·30	0	0	182·86	2·85	2·85	+1	+1
15·906	600·176	218·74	8·71	8·71	+3	+3	219·42	9·37	9·37	+5	+5
15·897	700·472	255·32	5·29	5·29	+3	+3	256·10	6·06	6·06	+4	+4
15·914	800·190	291·66	1·63	1·63	+3	+3	292·55	2·51	2·51	+4	+4
20·053	100·022	35·92	5·92	5·92	0	0	36·02	6·03	6·03	−1	−1
20·059	200·074	71·87	1·85	1·85	+2	+2	72·06	2·07	2·07	−1	−1
20·027	300·112	107·79	7·80	7·80	−1	−1	108·11	8·12	8·12	−1	−1
20·046	400·145	143·74	3·73	3·73	+1	+1	144·14	4·16	4·16	−2	−2
20·080	500·228	179·69	9·67	9·67	+2	+2	180·23	0·21	0·21	+2	+2
20·071	600·260	215·64	5·62	5·62	+2	+2	216·27	6·27	6·27	0	0
20·073	700·326	251·58	1·59	1·59	−1	−1	252·33	2·35	2·35	−2	−2
20·008	800·257	287·57	7·57	7·57	0	0	288·43	8·44	8·44	−1	−1
25·191	100·460	35·46	5·45	5·45	+1	+1	35·56	5·56	5·56	0	0
25·204	200·242	70·65	0·67	0·67	−2	−2	70·87	0·88	0·88	−1	−1
25·175	300·328	105·99	6·01	6·01	−2	−2	106·34	6·33	6·33	+1	+1
25·215	400·182	141·25	1·24	1·25	+1	0	141·69	1·67	1·67	+2	+2
25·240	500·224	176·57	6·55	6·56	+2	+1	177·10	7·09	7·09	+1	+1
25·230	600·074	211·82	1·82	1·82	0	0	212·47	2·46	2·46	+1	+1
25·226	700·117	247·16	7·15	7·15	+1	+1	247·91	7·90	7·90	+1	+1
25·231	800·092	282·44	2·46	2·46	−2	−2	283·32	3·31	3·31	+1	+1
30·534	100·964	34·99	5·00	5·01	−1	−2	35·08	5·11	5·11	−3	−3
30·540	200·690	69·56	9·58	9·58	−2	−2	69·79	9·79	9·79	0	0
30·547	301·763	104·59	4·62	4·63	−3	−4	104·93	4·94	4·95	−1	−2
30·544	400·182	138·75	8·76	8·77	−1	−2	139·20	9·18	9·18	+2	+2
30·582	500·395	173·44	3·50	3·50	−6	−6	174·00	4·02	4·03	−2	−3
30·535	599·731	207·98	7·99	7·99	−1	−1	208·63	8·61	8·62	+2	+1
30·615	702·230	243·49	3·49	3·49	0	0	244·24	4·22	4·22	+2	+2
30·521	800·703	277·70	7·74	7·73	−4	−3	278·53	8·58	8·57	−5	−4

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TABLE VIII (*continued*)

		λ_5					λ_6				
		$(n-1)\,10^6$			$O-C$		$(n-1)\,10^6$			$O-C$	
			Calculated					Calculated			
Temperature (° C)	Pressure (mm.)	Observed (O)	I	II	I	II	Observed (O)	I	II	I	II
12·074	100·307	37·23	7·25	7·24	−2	−1	37·31	7·30	7·30	+1	+1
12·058	200·139	74·32	4·33	4·32	−1	0	74·40	4·43	4·43	−3	−3
12·073	300·488	111·57	1·60	1·59	−3	−2	111·73	1·75	1·75	−2	−2
12·063	400·269	148·68	8·67	8·67	+1	+1	148·86	8·88	8·87	−2	−1
12·035	500·250	185·84	5·84	5·84	0	0	186·09	6·10	6·09	−1	0
12·055	600·380	223·03	3·04	3·04	−1	−1	223·34	3·35	3·34	−1	0
12·008	700·280	260·21	0·22	0·22	−1	−1	260·56	0·57	0·57	−1	−1
12·060	800·634	297·41	7·48	7·48	−7	−7	297·84	7·88	7·88	−4	−4
15·910	100·058	36·67	6·66	6·66	+1	+1	36·72	6·71	6·71	+1	+1
15·896	200·158	73·35	3·35	3·34	0	+1	73·46	3·45	3·44	+1	+2
15·907	300·203	110·02	0·01	0·01	+1	+1	110·17	0·16	0·16	+1	+1
15·902	400·406	146·78	6·74	6·74	+4	+4	146·95	6·94	6·94	+1	+1
15·901	500·294	183·36	3·37	3·36	−1	0	183·61	3·61	3·61	0	0
15·906	600·176	220·03	9·99	9·98	+4	+5	220·33	0·28	0·28	+5	+5
15·897	700·472	256·82	6·77	6·77	+5	+5	257·16	7·12	7·12	+4	+4
15·914	800·190	293·36	3·33	3·33	+3	+3	293·76	3·73	3·73	+3	+3
20·053	100·022	36·12	6·13	6·13	−1	−1	36·17	6·18	6·18	−1	−1
20·059	200·074	72·29	2·27	2·27	+2	+2	72·36	2·37	2·37	−1	−1
20·027	300·112	108·43	8·43	8·43	0	0	108·57	8·57	8·57	0	0
20·046	400·145	144·54	4·57	4·57	−3	−3	144·76	4·76	4·76	0	0
20·080	500·228	180·73	0·72	0·72	+1	+1	180·99	0·97	0·97	+2	+2
20·071	600·260	216·89	6·88	6·88	+1	+1	217·18	7·18	7·18	0	0
20·073	700·326	253·04	3·05	3·05	−1	−1	253·39	3·40	3·40	−1	−1
20·008	800·257	289·23	9·25	9·25	−2	−2	289·62	9·64	9·64	−2	−2
25·191	100·460	35·67	5·66	5·66	+1	+1	35·70	5·71	5·71	−1	−1
25·204	200·242	71·09	1·08	1·08	+1	+1	71·16	1·18	1·18	−2	−2
25·175	300·328	106·61	6·63	6·63	−2	−2	106·76	6·77	6·77	−1	−1
25·215	400·182	142·07	2·07	2·07	0	0	142·25	2·26	2·27	−1	−2
25·240	500·224	177·59	7·58	7·59	+1	0	177·82	7·82	7·83	0	−1
25·230	600·074	213·05	3·05	3·05	0	0	213·34	3·34	3·34	0	0
25·226	700·117	248·60	8·59	8·59	+1	+1	248·93	8·93	8·93	0	0
25·231	800·092	284·10	4·11	4·11	−1	−1	284·48	4·49	4·49	−1	−1
30·534	100·964	35·23	5·21	5·21	+2	+2	35·23	5·25	5·26	−2	−3
30·540	200·690	69·98	9·98	9·99	0	−1	70·07	0·08	0·08	−1	−1
30·547	301·763	105·25	5·23	5·24	+2	+1	105·39	5·38	5·38	+1	+1
30·544	400·182	139·61	9·57	9·57	+4	+4	139·80	9·76	9·76	+4	+4
30·582	500·395	174·51	4·51	4·51	0	0	174·74	4·75	4·75	−1	−1
30·535	599·731	209·24	9·20	9·20	+4	+4	209·54	9·48	9·49	+6	+5
30·615	702·230	244·95	4·91	4·91	+4	+4	245·26	5·24	5·24	+2	+2
30·521	800·703	279·34	9·36	9·35	−2	−1	279·71	9·74	9·73	−3	−2

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TABLE VIII (*continued*)

		λ_7					λ_8				
		$(n-1)\,10^6$					$(n-1)\,10^6$				
Temperature (° C)	Pressure (mm.)	Observed (O)	Calculated		$O-C$		Observed (O)	Calculated		$O-C$	
			I	II	I	II		I	II	I	II
12·074	100·307	37·38	7·39	7·39	−1	−1	37·45	7·45	7·45	0	0
12·058	200·139	74·62	4·62	4·62	0	0	74·74	4·74	4·73	0	+1
12·073	300·488	112·01	2·04	2·03	−3	−2	112·20	2·22	2·21	−2	−1
12·063	400·269	149·26	9·26	9·25	0	+1	149·49	9·49	9·49	0	0
12·035	500·250	186·55	6·57	6·57	−2	−2	186·87	6·87	6·86	0	+1
12·055	600·380	223·91	3·92	3·92	−1	−1	224·26	4·27	4·27	−1	−1
12·008	700·280	261·23	1·24	1·24	−1	−1	261·67	1·65	1·65	+2	+2
12·060	800·634	298·61	8·65	8·65	−4	−4	299·08	9·11	9·12	−3	−4
15·910	100·058	36·80	6·81	6·80	−1	0	36·85	6·86	6·86	−1	−1
15·896	200·158	73·63	3·63	3·63	0	0	73·73	3·75	3·75	−2	−2
15·907	300·203	110·45	0·44	0·44	+1	+1	110·63	0·62	0·61	+1	+2
15·902	400·406	147·34	7·32	7·32	+2	+2	147·56	7·55	7·55	+1	+1
15·901	500·294	184·08	4·09	4·08	−1	0	184·38	4·38	4·37	0	+1
15·906	600·176	220·86	0·85	0·85	+1	+1	221·23	1·20	1·20	+3	+3
15·897	700·472	257·78	7·78	7·78	0	0	258·23	8·19	8·19	+4	+4
15·914	800·190	294·52	4·49	4·49	+3	+3	294·99	4·95	4·95	+4	+4
20·053	100·022	36·26	6·27	6·27	−1	−1	36·33	6·33	6·33	0	0
20·059	200·074	72·56	2·56	2·56	0	0	72·67	2·67	2·67	0	0
20·027	300·112	108·86	8·85	8·85	+1	+1	109·03	9·02	9·02	+1	+1
20·046	400·145	145·13	5·14	5·14	−1	−1	145·35	5·36	5·37	−1	−2
20·080	500·228	181·44	1·43	1·43	+1	+1	181·74	1·72	1·72	+2	+2
20·071	600·260	217·73	7·73	7·73	0	0	218·09	8·08	8·08	+1	+1
20·073	700·326	254·04	4·05	4·05	−1	−1	254·46	4·45	4·45	+1	+1
20·008	800·257	290·39	0·38	0·39	+1	0	290·85	0·84	0·84	+1	+1
25·191	100·460	35·78	5·80	5·80	−2	−2	35·84	5·86	5·86	−2	−2
25·204	200·242	71·35	1·36	1·36	−1	−1	71·47	1·47	1·47	0	0
25·175	300·328	107·04	7·05	7·05	−1	−1	107·18	7·21	7·22	−3	−4
25·215	400·182	142·61	2·63	2·63	−2	−2	142·87	2·85	2·86	+2	+1
25·240	500·224	178·27	8·28	8·28	−1	−1	178·56	8·56	8·56	0	0
25·230	600·074	213·87	3·89	3·89	−2	−2	214·23	4·23	4·23	0	0
25·226	700·117	249·58	9·57	9·57	+1	+1	249·97	9·96	9·96	+1	+1
25·231	800·092	285·19	5·23	5·22	−4	−3	285·66	5·67	5·67	−1	−1
30·534	100·964	35·32	5·34	5·35	−2	−3	35·37	5·40	5·40	−3	−3
30·540	200·690	70·24	0·26	0·26	−2	−2	70·36	0·37	0·38	−1	−2
30·547	301·763	105·62	5·65	5·66	−3	−4	105·80	5·81	5·82	−1	−2
30·544	400·182	140·14	0·12	0·12	+2	+2	140·37	0·34	0·34	+3	+3
30·582	500·395	175·17	5·20	5·20	−3	−3	175·46	5·47	5·48	−1	−2
30·535	599·731	210·07	0·02	0·03	+5	+4	210·38	0·35	0·36	+3	+2
30·615	702·230	245·91	5·87	5·87	+4	+4	246·27	6·26	6·26	+1	+1
30·521	800·703	280·48	0·46	0·45	+2	+3	280·90	0·90	0·89	0	+1

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absorption lines in the infra-red, their influence in lowering the value of n in the visible region is negligible. We may therefore write

$$\begin{aligned}\Sigma_m[D_m/(\nu_m^2-\nu^2)] &= \Sigma_m[D'_m\{1+(\nu/\nu_m)^2+(\nu/\nu_m)^4+\ldots\}] \\ &= \Sigma_m[D'_m\{1+(\lambda_m/\lambda)^2+(\lambda_m/\lambda)^4+\ldots\}] \\ &= a_2+b_2\lambda^{-2}+c_2\lambda^{-4}+\ldots,\end{aligned}$$

where a_2, b_2 and c_2 are constants and λ is the wave-length *in vacuo* of the incident radiation. For most gases, and in particular for air in the visible spectrum, three terms of the expansion are sufficient to represent the observed facts with high accuracy, so that

$$(n^2-1) = [a_2+b_2\lambda^{-2}+c_2\lambda^{-4}]\,d. \tag{6·2}$$

This equation and the corresponding equation for the Lorenz-Lorentz expression (1·3), namely,

$$(n^2-1)/(n^2+2) = [a_3+b_3\lambda^{-2}+c_3\lambda^{-4}]\,d, \tag{6·3}$$

are based on theoretical relations concerned with the propagation of light through a transparent medium.

With a gas under normal conditions the value of $(n-1)$ is small, so that, if we put $(n-1)=r$, then the equations (6·1), (6·2) and (6·3), respectively, may be written in the following forms, since $(n^2-1)=2r+r^2=2r(1+r/2)$ and $(n^2-1)/(n^2+2)=(2r+r^2)/(3+2r+r^2)=2r(1-r/6)/3$:

$$r = [a_1+b_1\lambda^{-2}+c_1\lambda^{-4}]\,d, \tag{6·4}$$

$$r = (1-r/2)\,[a_2+b_2\lambda^{-2}+c_2\lambda^{-4}]\,d/2, \tag{6·5}$$

$$r = (1+r/6)\,[a_3+b_3\lambda^{-2}+c_3\lambda^{-4}]\,3d/2. \tag{6·6}$$

To a first approximation, since r is small, equations (6·5) and (6·6) reduce to the same form as (6·4), in which, for a given radiation, the refractivity is proportional to density, but it is also evident that if the measurements of refractivity of gases are of sufficiently high accuracy it may be possible to distinguish between the three relations.

Striking experimental confirmation of the Lorenz-Lorentz relation for gases was, in fact, obtained by Magri (1905), who made determinations of the refractivity of air at densities corresponding to pressures from about 1 to 200 atm., using a Jamin refractometer with the green line of mercury ($\lambda = 5461$ A). But Magri erroneously described his results as proving the constancy of the expression $(n^2-1)/(n^2+1)\,d$, and this expression has, in consequence, frequently been quoted as an independent empirical refraction constant, whereas, in fact, it appears simply to have been substituted by some curious error in place of the Lorenz-Lorentz expression $(n^2-1)/(n^2+2)\,d$ at the head of a column of figures actually calculated from this latter. We have therefore deemed it of sufficient importance to reprint the results of Magri's observations in the first three columns of Table IX, together with his quoted calculation of the values of $(n^2-1)/(n^2+1)\,d$ in the fourth column. In the next four columns of Table IX are

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given the results of our calculations, from Magri's own observational data, of the values of $(n^2-1)/(n^2+1)\,d$ and of the Gladstone and Dale, Newton-Laplace and Lorenz-Lorentz constants. It will be seen that the values given by Magri differ considerably from those of the formula quoted by him, whereas, apart from a few minor differences, they are identical with those of the Lorenz-Lorentz constant. It is evident, therefore, that Magri has misquoted the basis of his own calculations. This error appears hitherto to have escaped notice except for its tacit correction by Lorentz (1909, p. 146).

TABLE IX. MAGRI'S RESULTS ON AIR AT HIGH DENSITIES

Magri's observations and calculation				N.P.L. calculations from Magri's own observations			
$t°$ C	d	$(n-1)\,10^3$	$\frac{n^2-1}{n^2+1}\frac{1}{d}\times 10^6$	$\frac{n^2-1}{n^2+1}\frac{1}{d}\times 10^6$	$\frac{n-1}{d}\times 10^6$	$\frac{n^2-1}{d}\times 10^6$	$\frac{n^2-1}{n^2+2}\frac{1}{d}\times 10^6$
0	1·00	0·2929	195·3	292·9	292·9	585·9	195·3
14·6	14·84	4·338*	194·7	291·7	292·3	585·9	194·7
14·2	28·58	8·385	195·7	292·2	293·4	589·2	195·3
14·3	42·13	12·41	195·9	292·7	294·6	592·7	195·9
14·3	55·72	16·43	196·0	292·4	294·9	594·6	196·0
14·4	69·24	20·44	196·1	292·2	295·2	596·5	196·1
14·4	82·65	24·40	196·0	291·7	295·2	597·7	196·0
14·5	96·16	28·42	196·1	291·4	295·5	599·5	196·1
14·5	109·56	32·42	196·2	291·1	295·9	601·4	196·2
14·5	123·04	36·33	195·6	289·9	295·3	601·3	195·6
14·6	136·21	40·27	195·7	289·7	295·6	603·2	195·7
14·8	149·53	44·21	195·6	289·1	295·7	604·4	195·6
14·9	162·76	48·18	195·7	288·9	296·0	606·3	195·7
14·9	176·27	52·13	195·4	288·0	295·7	606·9	195·3
16·3	16·67	4·877	194·9	291·9	292·6	586·6	194·9
16·3	32·12	9·429	195·4	292·2	293·6	589·9	195·4
16·7	47·52	14·01	196·1	292·8	294·8	593·9	196·1
16·2	62·92	18·56	196·0	292·2	295·0	595·4	196·0
16·5	78·29	23·11	196·0	291·7	295·2	597·1	196·0
16·6	93·64	27·67	196·0	291·4	295·5	599·2	196·1
16·6	108·97	32·21*	196·0	290·8	295·6	600·7	196·0
16·8	124·30	36·73	195·7	290·1	295·5	601·9	195·7
16·7	139·60	41·28	195·7	289·6	295·7	603·6	195·7
16·9	154·78	45·78	195·6	289·0	295·8	605·1	195·6

* Values corrected for obvious misprints in original tables.

Table IX further shows that there is a marked superiority in the constancy of the Lorenz-Lorentz expression over that of the Gladstone and Dale and Newton-Laplace expressions, the values of which both tend to increase with density, although the rate of increase is not so great with the Gladstone and Dale as it is with the Newton-Laplace expression. Magri's results may therefore be regarded as providing strong confirmation of the Lorenz-Lorentz expression.

(*b*) *Relation between density, temperature and pressure.* We proceed now to a consideration of the relation between density, temperature and pressure of a gas, the theoretical basis for which is the Van der Waals' gas equation, or some empirical modification of

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this equation such as has been suggested by Berthelot (1907), particularly when pressures of about 1 atm. downwards are concerned. The Van der Waals' equation is

$$(p+a/v^2)\,(v-b) = RT,$$

where the symbols have the generally recognized significances. This can be written in the form

$$pv = RT+pb-a/v+ab/v^2,$$

which, for low pressures, becomes

$$pv = RT+(b-a/RT)\,p, \tag{6·7}$$

since the term involving $1/v^2$ is then very small and may be neglected, and v is replaceable by its equivalent from the limiting equation $pv = RT$. Equation (6·7) represents the isothermal corresponding to the temperature T on a diagram having values of pv as ordinates and values of p as abscissae; on such a diagram the slope of the line as given by $\frac{d(pv)}{dp}$ is a measure of the error from Boyle's law. If the gas is perfect, $\frac{d(pv)}{dp}$ is zero and the isothermal is parallel to the pressure axis.

Since from equation (6·7)

$$\frac{d(pv)}{dp} = b-\frac{a}{RT},$$

the error from Boyle's law is a function of temperature.

Equation (6·7) may be rewritten thus:

$$pv = RT\{1+(b-a/RT)\,p/RT\}. \tag{6·8}$$

In this equation the expression $(b-a/RT)/RT$ is equivalent to $\frac{1}{pv}\frac{d(pv)}{dp}$ at low pressures, and this may be regarded, following Berthelot, as a measure of the departure of a gas from the Avogadro-Ampère law, which states that the volumes occupied by a gram-molecule of any gas at a given temperature and pressure are equal. This error is also a function of temperature.

If we put $v = 1/d$ in equation (6·8), where d is the density of the gas, then, since $\frac{1}{pv}\frac{d(pv)}{dp}$ is small,

$$d = \frac{p}{RT}\left[1-\left(\frac{1}{pv}\frac{d(pv)}{dp}\right)p\right],$$

so that, if $T = T_0+t$, where T_0 is the melting-point of ice on the Kelvin scale,

$$d = \Delta p(1-\delta_t p)/(1+\alpha t), \tag{6·9}$$

in which $\Delta = 1/RT_0 =$ constant, $\alpha = 1/T_0 =$ theoretical expansion constant for a perfect gas, and $\delta_t = \left(\frac{1}{pv}\frac{d(pv)}{dp}\right)_t =$ departure from the Avogadro-Ampère law at temperature t° C.*

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* δ_t, as here defined, is opposite in sign to Mascart's constant, indicated by δ in equation (1·5).

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(*c*) *Derivation of the general interpolation equation.* We may now combine equation (6·9) with any one of the three equations (6·4), (6·5) and (6·6) and thus produce three alternative general interpolation equations for the refractivity of air in the visible spectrum. Confining attention to the equation (6·6), which is based on the Lorenz-Lorentz refraction constant and which is shown by the work of Magri to be the most satisfactory from the experimental standpoint, then

$$r = Kp(1-\delta_t p)\,(1+r/6)/(1+\alpha t), \tag{6·10}$$

in which $K = 3\Delta[a_3+b_3\lambda^{-2}+c_3\lambda^{-4}]/2 = A+B\lambda^{-2}+C\lambda^{-4}$, where A, B and C are constants.

As a first approximation to the value of r on the right-hand side of equation (6·10) we may write $K_m p/(1+\alpha t)$, where K_m is the mean value of K for the visible spectrum, and, since $r/6$ and δ_t are both small, we have finally

$$(n-1) = \left[A+\frac{B}{\lambda^2}+\frac{C}{\lambda^4}\right]\frac{p}{1+\alpha t}\left\{1+\left(\frac{K_m}{6(1+\alpha t)}-\delta_t\right)p\right\}. \tag{6·11}$$

Writing
$$\beta_t = K_m/6\,(1+\alpha t)-\delta_t, \tag{6·12}$$

equation (6·11) becomes identical in form with the interpolation equation (5·8), which was used for the final reduction of the refractivity observations, and which thus lends itself directly to the comparison of refractivity with density. It will be shown later that, over the range of temperature and pressure covered by our experiments, β_t may be expressed with sufficient accuracy for this purpose in the simple linear form

$$\beta_t = a-bt.$$

It can also be shown that, over a moderate temperature range such as is involved in our present experiments, the value of $K_m/6(1+\alpha t)$ in equation (6·12) can be written with sufficiently close approximation as a linear function of t, for

$$K_m/6(1+\alpha t) = K_m T_0/6T = K_m T_0/6\{T_m+(t-t_m)\} = K_m T_0\{1-(t-t_m)/T_m\}/6T_m,$$

where $T_m = T_0+t_m$, t_m being the mean temperature of the range investigated. Thus

$$K_m/6(1+\alpha t) = K_m T_0(1+t_m/T_m)/6T_m - K_m T_0 t/6T_m^2 = a'-b't,$$

where a' and b' are constants. Substituting for K_m the value of $0·3868\times10^{-6}$ from Table VII, and since $t_m = 21°$ C approximately, so that $T_m = 294°$ K, then

$$K_m 10^6/6(1+\alpha t) = 0·064-0·0002\,t. \tag{6·13}$$

Had equation (6·11) been based on the Gladstone and Dale relation then β_t would equal $-\delta_t$, and if on the Newton-Laplace relation then β_t would equal

$$[-K_m/2(1+\alpha t)-\delta_t],$$

so that it should be possible to distinguish between the various relationships provided that values of δ_t are known and that the value of β_t in equation (5·8) can be determined with sufficient accuracy.

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As regards the value of the theoretical coefficient of expansion to be used in (6·11), Keesom and Tuyn (1936) have recently given the value of $273{\cdot}14_4{}^\circ$ K as the freezing point of water on the Kelvin scale, based on the indications of the helium thermometer, so that $1/T_0 = 0{\cdot}0036611$, whereas Kinoshita and Oishi (1937) have given $273{\cdot}16_7{}^\circ$ K, for which $1/T_0 = 0{\cdot}0036608$. By adopting the sufficiently accurate rounded value of 0·003661 for the purpose of reductions of refractivity measurements, the actual value assigned to the freezing point of water on the Kelvin scale is unimportant so long as it remains within the limits defined by $T_0 \nless 1/0{\cdot}0036615$ or 273·112° K and $T_0 \ngtr 1/0{\cdot}0036605$ or 273·187° K.

It appears unlikely now that new determinations of the absolute zero of temperature will lead to a value outside these limits, so that the value accepted for α is not likely to be subject to any change affecting the fourth significant figure. It is for this reason that we have preferred to express the interpolation equation in the form

$$(n-1) = Kp/(1+\alpha t)$$

in which the value of α may be regarded as already established with sufficient accuracy for its purpose, rather than in the ideal form

$$(n-1) = Kp/T = Kp/(T_0+t)$$

in which the last digit in the value of T_0 is still subject to some small degree of indeterminacy in a four-figure approximation.

(*d*) *Relationships derived from compressibility measurements.* In order to proceed further with the comparison of the various relationships between refractive index and density of gases, it is necessary to calculate values of δ_t from the equation

$$\delta_t = (b-a/RT)/RT$$

derived from equation (6·8), and this can be done if the appropriate values of R, a and b are substituted from Van der Waals' equation. But it has been shown by Berthelot (1907) that the values for δ_t at low pressures obtained in this manner do not agree with the experimental facts obtained from compressibility measurements on gases at low pressures. Following Berthelot, if Van der Waals' equation is transferred to the form employing the "reduced" variables π, v and θ, where $\pi = p/p_c$, $v = v/v_c$ and $\theta = T/T_c$, p_c, v_c and T_c being the critical constants of the gas, then the equation becomes a characteristic equation for all gases, which may be written as

$$(\pi+3/v^2)\,(v-1/3) = 8\theta/3,$$

and from which the departure from Boyle's law is given by

$$\frac{d(\pi v)}{d\pi} = \frac{1}{3}\left(1-\frac{27}{8}\frac{1}{\theta}\right).$$

The values calculated from this expression were compared by Berthelot with the experimental determinations of the departure from Boyle's law for many gases at

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different temperatures, and he found a systematic disagreement. According to Berthelot the best empirical relation for the departure from Boyle's law in the reduced form is

$$\frac{d(\pi v)}{d\pi}=\frac{1}{4}\left(1-\frac{6}{\theta^2}\right),$$

from which he derived the characteristic equation

$$(\pi+16/3\theta v^2)\,(v-1/4)=32\theta/9.$$

In normal variables Berthelot's equation corresponds to an equation of the Van der Waals' type, as modified by Clausius, namely,

$$(p+a/Tv^2)\,(v-b)=RT,$$

in which the quantity a, originally introduced as a constant by Van der Waals to take account of molecular attraction, is made dependent on temperature.

The error from the Avogadro-Ampère law derived from Berthelot's empirical equation is

$$\frac{1}{\pi v}\frac{d(\pi v)}{d\pi}=\frac{9}{128\theta}\left(1-\frac{6}{\theta^2}\right). \tag{6·14}$$

By converting the left-hand side of equation (6·14) to normal variables, it can be shown that

$$\frac{1}{\pi v}\frac{d(\pi v)}{d\pi}=p_c\left(\frac{1}{pv}\frac{d(pv)}{dp}\right),$$

so that

$$\delta_t=\left(\frac{1}{pv}\frac{d(pv)}{dp}\right)_t=\frac{1}{p_c}\left[\frac{9T_c}{128T}\left(1-\frac{6T_c^2}{T^2}\right)\right], \tag{6·15}$$

where $T=(T_0+t)$ and $T_c=(T_0+t_c)$. Thus, if the critical pressure and critical temperature of a gas are known the values of δ_t at any temperature may be easily calculated by means of equation (6·15).

The best mean values for the critical constants of air as given by Germann and Pickering (1928) are $t_c=-140{\cdot}7^\circ$ C and $p_c=37{\cdot}2$ atm. Substituting these values of the critical constants in (6·15) the following values of δ_t were calculated for the mean temperatures of the first five series of refractivity measurements:

t° C	T° K	$\delta_t\times10^6$	$(-0{\cdot}463+0{\cdot}0103\,t)$
12·1	285·2	−0·34	−0·34
15·9	289·0	−0·30	−0·30
20·1	293·2	−0·25	−0·26
25·2	298·3	−0·20	−0·20
30·6	303·7	−0·15	−0·15

The values of T were calculated from the expression (T_0+t), putting $T_0=273{\cdot}1^\circ$ K.

Over the range of temperature indicated, δ_t is very closely a linear function of t, and as shown above can be represented by the equation

$$\delta_t\times10^6=-0{\cdot}463+0{\cdot}0103\,t, \tag{6·16}$$

derived by a least squares method from the individually calculated values.

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Combining equations (6·13) and (6·16), we obtain

$$\beta_t \times 10^6 = \{K_m/6(1+\alpha t)-\delta_t\}\, 10^6 = 0{\cdot}527-0{\cdot}0105\, t. \tag{6·17}$$

This is the justification for the assumption made in computing our final interpolation equation, that β_t may be assumed to be expressible as a linear function of t. The constants in equation (6·17) can be compared directly with those derived from the refractivity measurements, which gave

$$\beta_t \times 10^6 = 1{\cdot}049-0{\cdot}0157\, t.$$

Qualitatively, the agreement is moderately good, for there is fair accordance both with the sense and magnitude of the variation with temperature, especially having regard to the smallness of the magnitudes concerned. The magnitudes of the experimental values of β_t and of the expression derived through the Lorenz-Lorentz relation from δ_t are not in such good agreement; but the discordance between them would be increased if the expression containing δ_t had been derived through either the Gladstone and Dale or the Newton-Laplace relations.

In explanation of the disparity which remains, it is pertinent to mention that Berthelot shows that the observed value of the departure from Boyle's law for air is also not in such good agreement with the value calculated from his characteristic equation as it is with other gases which he investigated. This may be largely due to the fact that air is not a pure gas, and the values of the critical constants for air have not the same definite physical significance as they have for pure gases.

In support of this explanation it can be shown that the values of β_t derived from actual compressibility measurements on air at low pressures are much closer to the values obtained from the refractivity measurements. Thus, for instance, Rayleigh (1905) has measured δ for air at 11° C for expansions from 0·5 to 1 atm. and gives the value of $-0{\cdot}00046$ per atm., corresponding to $-0{\cdot}60_5 \times 10^{-6}$ per mm. Berthelot (1907) quotes the value of $-0{\cdot}00040$ per atm. at 16° C, as measured by himself and Sacerdote, corresponding to $-0{\cdot}52_6 \times 10^{-6}$ per mm. Assuming these two values and a linear change of δ with t over the limited range of temperature of 5° C, then

$$\delta_t \times 10^6 = -0{\cdot}779+0{\cdot}0158\, t,$$

and, combining this with equation (6·13), we get

$$\beta_t \times 10^6 = \{K_m/6(1+\alpha t)-\delta_t\}\, 10^6 = 0{\cdot}843-0{\cdot}0160\, t. \tag{6·18}$$

The agreement with the refractivity measurements is now much more striking, although the calculated and observed values of β_t still show some discordance which, as before, would be increased if the Gladstone and Dale or the Newton-Laplace relations were used instead of the Lorenz-Lorentz in the derivation of β_t.

Another comparison with observed results of compressibility measurements of air can be made through the work of Holborn and Schultze, whose final results are quoted by Holborn and Otto (1924). Holborn and Schultze determined the isothermals of

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dry, CO_2-free air at temperatures from 0 to 200° C and at pressures up to 100 atm. Their results may be summarized by means of the equation

$$pv = A + Bp + Cp^2,$$

where p is expressed in metres of mercury and A, B and C have the following values at various temperatures:

t° C	A	$B \times 10^3$	$C \times 10^6$
0	1·00080	−0·79333	+5·2222
50	1·18397	−0·18517	+3·7611
100	1·36713	+0·20933	+3·1000
150	1·55030	+0·50000	+2·3333
200	1·73317	+0·72317	+1·8167

Since $\left(\dfrac{1}{pv}\dfrac{d(pv)}{dp}\right)_t = \left(\dfrac{B+2Cp}{A+Bp+Cp^2}\right)_t$, we have $\delta_t = (B/A)_t$ when $p = 0$ and

$$\delta_t = [(B+2C)/(A+B+C)]_t$$

when $p = 1$ m. It is found that the values of δ_t change very little over the range of pressure from 0 to 1 m. and we may therefore accept the following mean observed values of δ_t per mm. as applying to this whole range of pressure:

t° C.	$\delta_t \times 10^6$ (observed)	$\delta_t \times 10^6$ (calculated)
0	−0·788	−0·761
50	−0·153	−0·210
100	+0·156	+0·166
150	+0·324	+0·368
200	+0·418	+0·395

The values described above as observed are those which have been directly derived from the observed isothermals, and it can be shown that they are sufficiently well represented by the equation

$$\delta_t \times 10^6 = -0{\cdot}761 + 0{\cdot}012{,}77\,t - 0{\cdot}000{,}034{,}94\,t^2.$$

The calculated values from this equation, which was obtained by a least squares method, are given above for comparison with the observed values.

Using this equation the values of δ_t given below were calculated for the five mean temperatures of the refractivity measurements:

t° C	$\delta_t \times 10^6$
12·1	−0·61
15·9	−0·57
20·1	−0·52
25·2	−0·46
30·6	−0·40

These values exactly fit the linear equation

$$\delta_t \times 10^6 = -0{\cdot}751 + 0{\cdot}0115\,t, \tag{6·19}$$

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which applies to the limited range of temperature from 12·1 to 30·6° C. By combining equations (6·19) and (6·13), we get

$$\beta_t\times 10^6=\{K_m/6(1+\alpha t)-\delta_t\}\,10^6=0{\cdot}815-0{\cdot}0117\,t. \qquad (6{\cdot}20)$$

Table X presents for comparison the calculated values of $\{K_m/6(1+\alpha t)-\delta_t\}\,10^6$ as derived from the equations (6·17), (6·18) and (6·20), together with the directly observed values of $\beta_t\times 10^6$ obtained from the refractivity measurements on air. On the average the best agreement with our refractivity measurements is obtained from the isothermals of Holborn and Schultze, the mean values of β at 20·8° C being $0{\cdot}72\times 10^{-6}$ and $0{\cdot}57\times 10^{-6}$ per mm. respectively.

Table X. Values of $\beta_t\times 10^6$ derived from various sources

	Values of $\beta_t\times 10^6$ derived from $\left(\frac{1}{6}\frac{K_m}{1+\alpha t}-\delta_t\right)10^6$					
Source	12·1° C	15·9° C	20·1° C	25·2° C	30·6° C	Mean 20·8° C
Berthelot's empirical relation for pure gases: $\frac{1}{\pi v}\frac{d(\pi v)}{d\pi}=\frac{9}{128\theta}\left(1-\frac{6}{\theta^2}\right)$	0·40	0·36	0·32	0·26	0·21	0·31
Compressibility measurements on air by Rayleigh, Berthelot and Sacerdote at 11 and 16° C	0·65	0·59	0·52	0·44	0·35	0·51
Isothermals of air from 0 to 200° C at pressures up to 100 atm., determined by Holborn and Schultze	0·67	0·63	0·58	0·52	0·46	0·57
Refractivity measurements of air (N.P.L., directly observed)	0·86	0·80	0·73	0·65	0·57	0·72

Comparing Table X with Table VI it is at once apparent that, although there are appreciable differences between the values in Table X derived from various sources, the individual values of β_t in Table VI include entries, particularly for λ_4 and λ_5, which are practically identical with the values derived from the determinations of Holborn and Schultze. A reference to Table IV shows that the variations in the individual values of β calculated from the refractivity measurements without regard to any temperature relationship are considerably greater, and actually extend over a range which includes all the values derived from compressibility measurements on air.

Having regard to the high experimental accuracy of the refractivity determinations exhibited by Table VIII it is evident that very small changes in the magnitude and distribution of observational errors are sufficient to cause relatively large variations in the derived values of β. In our view, therefore, it is not surprising that our values for β_t should differ slightly from those deduced from compressibility measurements on air, but rather, remembering the somewhat limited range of temperature and pressure covered by our experiments, we consider that the agreement found must be regarded

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as a very satisfactory confirmation of the assumed relationship between the refractive index, temperature and pressure of air.

As a check on the closeness of the agreement actually established we have carried out a further calculation in which the values of β_t, based on the compressibility measurements of Rayleigh, Berthelot and Sacerdote, were employed in an interpolation equation of similar form to equation (5·8). The maximum difference at 800 mm. pressure between the values of the refractive index as calculated from this equation and the corresponding values calculated from equation (5·12) amounted only to $0{\cdot}02_4 \times 10^{-6}$.

We consider, therefore, that the relation connecting temperature, pressure and refractive index of gases, including air, may be regarded as established; and in spite of the difficulty mentioned above relating to the exact determination of β_t, we believe that precise measurements of refractivity, if carried out over a greater range of temperature and pressure than was possible with our apparatus, would afford information on the characteristic behaviour of gases at low pressures at least as accurate as direct compressibility measurements.

7. Refractivity of air under ordinary atmospheric conditions

(*a*) *Determinations of refractivity of moist*, CO_2*-free air*. Determinations of the refractivity of moist CO_2-free air were made on very similar lines to those already described for dry air, except that they all referred to a total pressure of about 760 mm. and a temperature of about 29·5° C.

In order to control the amount of water vapour present in the air contained in étalon L_{10}, the distilled water flask shown in fig. 3 was used. This flask contained distilled water which had been rendered air-free by boiling at a reduced pressure, and was immersed in a stirred water-bath. When it was desired to admit water vapour to the étalon, the latter was first evacuated and then connected to the flask. Observation of Brewster's fringes showed that further entry of vapour to the étalon ceased after a few minutes, and the pressure of the amount admitted was obtained, by reference to tables (Osborne and Meyers 1934, Table 2) of the saturated vapour pressure of water, from a knowledge of the temperature of the water-bath, which was assumed to be the same as that of the distilled water inside the flask.

Dry, CO_2-free air was then admitted to the étalon in the usual manner until the desired total pressure of 760 mm. was indicated by the barometer gauge. Knowing the total pressure of the mixture and the partial pressure of the water vapour, the partial pressure of the dry, CO_2-free air was derived.

It was important to ensure that the temperature of the water in the flask was lower than that of any other point in the system to which it was connected, in order to prevent local condensation of vapour and the consequential disturbance of vapour pressure in

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the system. Under the conditions of temperature in which these experiments were carried out this safeguard was automatically provided by the cooling of the water-bath, to a temperature of from 3 to 4° C below that of its surroundings, which occurred as a result of comparatively rapid evaporation at the free surface of the water contained therein. This cooling effect was probably enhanced by bubbling air through the water-bath as a method of stirring it.

As the stirred water-bath, surrounding the flask containing distilled water, was not necessarily maintained at the same temperature during the filling operation as it was during the subsequent determination of refractivity, care was taken to leave the flask in communication with étalon L_{10} during the whole of the intervening period. The temperature of the bath was taken, by means of two mercury-in-glass thermometers, at the beginning and end of the photographic period concerned with the recording of the fringes corresponding to the air-filled condition of L_{10}, and the mean of their corrected readings was taken to represent the temperature of the water inside the flask.

Determinations of the total fringe displacement due to moist air were made by preliminary experiments in which the rate of entry of water vapour into the étalon L_{10}, previously evacuated, was controlled so that the complete displacement could be actually counted in several radiations, the whole displacement in mercury green light being less than twenty fringes for the vapour pressures used. By assuming that the law of partial pressures holds for the admixture of unsaturated water vapour and dry air, the total displacement for moist air at pressures of about 760 mm. could then be calculated from the information already available from the determinations of refractivity of dry air.

Table XI gives the results obtained from the four determinations of refractivity of moist, CO_2-free air made in the second part of the series of April 1937. The data concerning the conditions of the air are given in the second column, where t, p are the temperature and pressure of the moist air in étalon L_{10}, θ is the mean temperature of the water-bath surrounding the distilled water flask (see fig. 3) in which the saturated vapour pressure, as obtained from Osborne and Meyers' tables (1934), is f, and $(p-f)$ is the partial pressure of the dry, CO_2-free air as derived from the known values of p and f. The difference between the observed refractivities of moist air under the conditions (t, p) and the calculated refractivities of dry, CO_2-free air under the conditions $[t, (p-f)]$, as derived from the final interpolation equation (5·12), gives the refractivities for water vapour under the conditions (t, f).

(*b*) *Refractivity of water vapour.* As in the case of air, the refractivity of water vapour under the conditions (t, f) may be expressed by means of the relation

$$(n'_{t,f}-1) = K'f(1+\beta'_t f)/(1+\alpha t), \qquad (7{\cdot}1)$$

in which $K' = A' + B'\lambda^{-2}$, A' and B' being constants in a two-term Cauchy equation, which expresses the dispersion of water vapour with sufficient accuracy when f is small,

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TABLE XI. DETERMINATIONS OF REFRACTIVITY OF MOIST, CO_2-FREE AIR

(The values of refractivity shown are multiplied by 10^6)

Exp.	Moist air conditions		λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8
1	t = 29·405° C	Moist air at t, p	261·922	262·721	263·427	264·227	264·976	265·346	266·020	266·460
	θ = 25·29	Dry air at $t, (p-f)$	254·912	255·631	256·315	257·089	257·810	258·160	258·824	259·231
	f = 24·142 mm.	Water vapour at t, f	7·010	7·090	7·112	7·138	7·166	7·186	7·196	7·229
	p = 760·400									
	$p-f$ = 736·258	$K' \times 10^6$	0·3214	0·3251	0·3261	0·3273	0·3286	0·3295	0·3300	0·3315
2	t = 29·425° C	Moist air at t, p	261·780	262·591	263·282	264·025	264·838	265·205	265·887	266·323
	θ = 25·76	Dry air at $t, (p-f)$	254·568	255·287	255·970	256·742	257·462	257·812	258·476	258·881
	f = 24·825 mm.	Water vapour at t, f	7·212	7·304	7·312	7·283	7·376	7·393	7·411	7·442
	p = 760·140									
	$p-f$ = 735·315	$K' \times 10^6$	0·3216	0·3257	0·3261	0·3248	0·3289	0·3297	0·3305	0·3319
3	t = 29·576° C	Moist air at t, p	261·663	262·432	263·118	263·925	264·691	265·060	265·725	266·149
	θ = 26·79	Dry air at $t, (p-f)$	253·930	254·647	255·329	256·099	256·817	257·166	257·828	258·233
	f = 26·383 mm.	Water vapour at t, f	7·733	7·785	7·789	7·826	7·874	7·894	7·897	7·916
	p = 760·224									
	$p-f$ = 733·841	$K' \times 10^6$	0·3246	0·3268	0·3270	0·3286	0·3306	0·3314	0·3315	0·3323
4	t = 29·509° C	Moist air at t, p	261·783	262·563	263·256	264·010	264·808	265·195	265·878	266·288
	θ = 25·85	Dry air at $t, (p-f)$	254·530	255·248	255·931	256·704	257·423	257·773	258·437	258·842
	f = 24·958 mm.	Water vapour at t, f	7·253	7·315	7·325	7·306	7·385	7·422	7·441	7·446
	p = 760·367									
	$p-f$ = 735·409	$K' \times 10^6$	0·3218	0·3246	0·3250	0·3242	0·3277	0·3293	0·3302	0·3304
		$K' \times 10^6$ (mean)	0·3224	0·3256	0·3260	0·3262	0·3289	0·3300	0·3305	0·3315

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and λ being the wave-length *in vacuo*, expressed in microns. The value of β'_t* for water vapour at the mean temperature of these experiments is 24×10^{-6}, as derived by calculation from Berthelot's characteristic equation for gases at low pressures, and $\alpha = 0{\cdot}003661$. The calculated values of $K' \times 10^6$ as given by equation (7·1) are shown in Table XI, together with the mean value for each radiation. The eight mean values were used to calculate the following values of A' and B' by a least squares method,

$$A' = 0{\cdot}3159 \times 10^{-6} \quad \text{and} \quad B' = 2{\cdot}963 \times 10^{-9}.$$

Hence
$$K' \times 10^6 = 0{\cdot}3159 + 0{\cdot}002{,}963\,\lambda^{-2}. \tag{7·2}$$

The average departure of the mean values of K' given in Table XI from the values calculated by means of equation (7·2) is $\pm 0{\cdot}0005 \times 10^{-6}$ or 1 part in 600.

Thus, the final form of equation (7·1) is

$$(n'_{t,f} - 1)\,10^6 = \left[0{\cdot}3159 + \frac{0{\cdot}002963}{\lambda^2}\right] \frac{f(1+\beta'_t f)}{1 + 0{\cdot}003661\,t}. \tag{7·3}$$

The experiments from which this interpolation equation was derived were made in moist air at about 29·5° C for which the relative humidity was about 80 %. Equation (7·3) is therefore only intended for use under conditions of vapour pressure normally existing in temperate climates, where the average value of f is about 10 mm., the maximum value rarely exceeding 20 mm. The factor $(1+\beta'_t f)$ can for most ordinary purposes be neglected.

(*c*) *Interpolation equation for atmospheric air.* It is of practical utility to derive a general interpolation equation which will serve for calculating the refractivity of moist air containing a proportion of 0·03 % by volume of CO_2—this being generally regarded as the normal amount of CO_2 present in the open air and in well-ventilated rooms. Air containing this proportion of CO_2 is usually described as "normal"; it has a slightly higher refractivity than CO_2-free air under the same conditions of temperature and pressure. Moist air has a lower refractivity than dry air under the same conditions of temperature and pressure, and it is the purpose of the following calculation to derive a general interpolation equation for the refractivity of moist, normal air, the vapour pressure of which is measured by hygrometric methods.

Since the amount of CO_2 present in normal air is very small it is sufficiently accurate for our purpose to select the result of any previously recorded determination of the

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* The value of $-\delta_t$ for water vapour, as calculated from equation (6·15), was actually used instead of β'_t, the difference between $-\delta_t$ and β'_t being unimportant for the purpose of deriving K' in equation (7·1). The same approximation was made for CO_2 in the next section of this paper. Values of the critical constants, from Germann and Pickering (1928) are

	$t°$ C	p_c atm.
Water vapour	374·0	$217{\cdot}7_2$
Carbon dioxide	31·1	73·0

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refractivity of CO_2. According to Perreau (1896) the refractivity of CO_2 at 0° C and 760 mm. is given by

$$(n''-1)\,10^6 = 442\cdot 1+2\cdot 829\,\lambda_N^{-2},$$

where λ_N is the wave-length in normal air expressed in microns.

Using this equation the value of K'' for CO_2 may be calculated from

$$K'' = (n''-1)/760\,(1+760\beta_0''),$$

where $\beta_0'' = 9\cdot 1\times 10^{-6}$ for this gas,* as derived from Berthelot's characteristic equation for gases. Thus

$$K''\times 10^6 = 0\cdot 5777+0\cdot 003{,}697\,\lambda_N^{-2}.$$

But for dry, CO_2-free air, by equation (5·12)

$$K\times 10^6 = 0\cdot 378{,}065+0\cdot 002{,}141{,}0\,\lambda^{-2}+0\cdot 000{,}017{,}94\,\lambda^{-4}.$$

If the value of K for dry, normal air is denoted by K_N, therefore

$$\begin{aligned} K_N &= 0\cdot 9997\,K+0\cdot 0003\,K'' \\ &= 0\cdot 378{,}125+0\cdot 002{,}141{,}4\,\lambda^{-2}+0\cdot 000{,}017{,}93\,\lambda^{-4}, \end{aligned} \tag{7·4}$$

since λ may be substituted for λ_N in the expression for $0\cdot 0003\,K''$ without appreciable error.

It is assumed in deriving the expression for K_N given by equation (7·4) that the value of β_t for normal air is negligibly different from that for CO_2-free air—an assumption which is justifiable owing to the small quantity of CO_2 concerned.

If, now, $(n_{t,p,f}-1)$ represents the refractivity of atmospheric air containing water vapour at pressure f mm., then

$$(n_{t,p,f}-1) = \frac{K_N(p-f)\,\{1+\beta_t(p-f)\}}{1+\alpha t}+\frac{K'f(1+\beta_t' f)}{1+\alpha t}, \tag{7·5}$$

where $\alpha = 0\cdot 003661$, $\beta_t = (1\cdot 049-0\cdot 0157\,t)\,10^{-6}$, $\beta_t' = 27\times 10^{-6}$ at a mean temperature of 20° C, and K' = value of K for water vapour.

By expanding equation (7·5) and collecting terms, we have

$$(n_{t,p,f}-1) = \frac{K_N p(1+\beta_t p)}{1+\alpha t}-\frac{f\{(1+2\beta_t p)\,K_N-K'\}}{1+\alpha t}+\frac{f^2(K_N\beta_t+K'\beta_t')}{1+\alpha t}.$$

It can be shown that the term in f^2 may be neglected for all practical purposes within the range of normal variations of atmospheric conditions.

Also, when $t = 20°$ C and $p = 760$ mm.

$$K_N(1+2\beta_t p)-K' = [0\cdot 0624-0\cdot 000{,}680\,\lambda^{-2}]\,10^{-6}. \tag{7·6}$$

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* See footnote p. 50.

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For the purpose of evaluating the above expression it was found convenient to transform equation (7·4) into the approximately equivalent two-term Cauchy equation, since the value of K' was expressed in this form, and under this transformation

$$K_N \times 10^6 = 0{\cdot}3779 + 0{\cdot}002{,}280\,\lambda^{-2}.$$

It was also found that the value given by (7·6) may be regarded as constant within the ranges of temperature and pressure of 10–30° C and 720–800 mm. respectively, without introducing any appreciable errors in the calculations for which it is used. Thus, the equation for the refractivity of moist, normal air is reduced to the following form:

$$(n_{t,\,p,\,f}-1)\,10^6 = \left[0{\cdot}378{,}125 + \frac{0{\cdot}002{,}141{,}4}{\lambda^2} + \frac{0{\cdot}000{,}017{,}93}{\lambda^4}\right] \times \frac{p\{1+(1{\cdot}049-0{\cdot}0157\,t)\,p\times 10^{-6}\}}{1+0{\cdot}003661\,t} - \left[0{\cdot}0624 - \frac{0{\cdot}000{,}680}{\lambda^2}\right]\frac{f}{1+0{\cdot}003661\,t}. \qquad (7{\cdot}7)$$

This equation is applicable for the ranges $t = 10$–$30°$ C and $p = 720$–800 mm.

The actual values of the corrective term in equation (7·7) per mm. of water vapour present are, for the eight radiations given in Table I:

λ_1	λ_2	λ_3	λ_4	λ_5
$-0{\cdot}0567$	$-0{\cdot}0563$	$-0{\cdot}0560$	$-0{\cdot}0557$	$-0{\cdot}0553$

λ_6	λ_7	λ_8	λ_{mean}
$-0{\cdot}0553$	$-0{\cdot}0550$	$-0{\cdot}0548$	$-0{\cdot}0556 \times 10^{-6}$

For most purposes it is sufficiently accurate to employ the mean value of $-0{\cdot}0556\times 10^{-6}$ per mm. of water vapour for all wave-lengths within the visible spectrum, the errors in refractivity for a value of $f = 10$ mm. being approximately $\pm 0{\cdot}01\times 10^{-6}$ at the limits of the range.

8. COMPARISONS WITH EARLIER RESULTS

(*a*) *General.* Tilton (1934) gives as the general average value of the refractivity of dry air, at 0° C and 760 mm., for the D line of sodium:

$$(n_D - 1)\,10^6 = 292{\cdot}5_4.$$

This is the mean value determined from forty determinations recorded by different observers between 1857 and 1932.

Conventionally, the wave-length of the D line relates to the mid-point of the sodium yellow doublet D_1D_2, the value of which in normal air is 5892·946 A, as given by Fowler (1922), corresponding to the value 5894·58 A *in vacuo*. The value of $(n_D - 1)\,10^6$ at 0° C and 760 mm. derived from the results of this investigation by means of the interpolation equations (5·12) and (7·7) is, then, 292·36 for dry, CO_2-free air and 292·41 for dry air containing 0·03 % of CO_2. The mean of these two calculated values is

$$(n_D - 1)\,10^6 = 292{\cdot}38,$$

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and this agrees fairly closely with the general average of the forty other determinations quoted above, which include without distinction values for air both with and without CO_2.

An examination of Tilton's collected results by an elementary statistical method (Sears 1909), dependent, like the use of the arithmetical mean, on treating the individual results as of equal weight, shows that the position of the arithmetical mean is displaced owing to the presence of a few abnormally high values, and that, in fact, the most probable value derived from the whole collection is $(n_D-1)\,10^6 = 292{\cdot}3_5$, which is in even closer agreement with the value found in the present investigation. Moreover, this statistical examination produces a probability curve, closely resembling the theoretical "cocked hat" curve, which shows no evidence of the double maximum which would be expected if a periodical variation such as that suggested by Tilton were present.

(*b*) *Recent results of other observers in the visible spectrum.* A more detailed comparison will now be made with the results of Meggers and Peters (N.B.S.) (1918–19), Pérard (B.I.P.M.) (1934), and Kösters and Lampe (P.T.R.) (1934), which have been selected for this purpose from among recent determinations for the following reasons. The work of Meggers and Peters, carried out in 1918 and covering a range from 2218 to 9000 A, has come to be regarded as a classical determination among spectroscopists, and the results of this work have been generally used during the past 20 years for the purpose of reducing wave-lengths determined in air to vacuum conditions, this being part of the process of conversion to the wave-numbers which are required in the analysis of spectra. Since 1918 there have been only two determinations of the refractivity of air confined to the visible spectrum alone, those of Pérard and Kösters and Lampe, which have therefore been selected for detailed comparisons in addition to those of Meggers and Peters. Other determinations in this period have been concerned with a part only of the visible spectrum and extend either into the infra-red or the ultra-violet. The determinations of this kind which we have noticed include those of Traub (1920), Stoll (1922), Rusch (1923), Quarder (1924), Tausz and Görlacher (1931), Krönjager (1935) and Bender (1938).*

The results of Meggers and Peters are expressed in terms of the refractivity of dry air, at 0, 15 and 30° C and at 760 mm. pressure, containing an unspecified amount of CO_2, by means of the following equations:

$$0^\circ\text{ C: } (n-1)\,10^6 = 287{\cdot}566 + 1{\cdot}3412\,\lambda_N^{-2} + 0{\cdot}03777\,\lambda_N^{-4},$$
$$15^\circ\text{ C: } (n-1)\,10^6 = 272{\cdot}643 + 1{\cdot}2288\,\lambda_N^{-2} + 0{\cdot}03555\,\lambda_N^{-4},$$
$$30^\circ\text{ C: } (n-1)\,10^6 = 258{\cdot}972 + 1{\cdot}2259\,\lambda_N^{-2} + 0{\cdot}02576\,\lambda_N^{-4}.$$

In these equations λ_N is the wave-length in normal air at 15° C and 760 mm. expressed in terms of microns (range $0{\cdot}2218$–$0{\cdot}9000\mu$). From these equations Meggers and

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* Bender's paper appeared while the present paper was in proof.

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Peters deduce that the value of the optical temperature coefficient is a function of wave-length, and that, within the range of their observations, the refractivity of air at any temperature for any particular wave-length can be obtained from the measurements at 0° C by means of the relation

$$(n_t-1) = (n_0-1)/\{1+(\alpha+3\lambda_N^{-3}\times 10^{-6})\,t\} = (n_0-1)/(1+\alpha' t),$$

where $\alpha = 0\cdot00367$ and λ_N is expressed in microns.

For the eight radiations mentioned in Table I we find the following values of α', $(n_{15}-1)\,10^6$ and $(n_{20}-1)\,10^6$, as derived from this relation and the equation for the refractivity at 0° C:

Radiation	α'	$(n_{15}-1)\,10^6$	$(n_{20}-1)\,10^6$
λ_1	0·003681	275·793	271·065
λ_2	0·003685	276·485	271·741
λ_3	0·003688	277·157	272·397
λ_4	0·003693	277·921	273·142
λ_5	0·003697	278·647	273·850
λ_6	0·003699	279·003	274·198
λ_7	0·003704	279·680	274·858
λ_8	0·003706	280·103	275·271

In Table XII the values of $(n_{15}-1)\,10^6$ and $(n_{20}-1)\,10^6$ given above have been corrected to the CO_2-free condition by assuming that they refer to air containing 0·03 % of CO_2. The corrections for this purpose were determined from a comparison of our interpolation equations (5·12) and (7·7), referring respectively to dry, CO_2-free air and dry atmospheric air, the average value of the correction to the refractive index at 15° C and at 20° C being $-0\cdot04_4\times 10^{-6}$ and $-0\cdot04_3\times 10^{-6}$ respectively.

Pérard's results refer to dry, CO_2-free air and are expressed in terms of the following interpolation equation

$$(n_{t,p}-1)\,10^6 = \left[288\cdot023+\frac{1\cdot4783}{\lambda_N^2}+\frac{0\cdot03161}{\lambda_N^4}\right]\frac{p(1+\beta p)}{760(1+760\beta)}\,\frac{1}{1+\alpha t},$$

which also relates to exactly the same range of the visible spectrum as the present investigation. In this equation $\beta = 2\cdot40\times 10^{-6}$/mm. and $\alpha = 0\cdot003716/1°$ C (determined for the range of temperature 0–100° C); the values calculated directly from it at 15 and 20° C and at 760 mm. pressure are given in Table XII.

Kösters and Lampe's results also refer to dry, CO_2-free air for the visible spectrum (exact range not specified) and are expressed thus:

$$(n_{t,p}-1)\,10^6 = \left[268\cdot036+\frac{1\cdot476}{\lambda^2}+\frac{0\cdot01803}{\lambda^4}\right]\frac{p}{760}\,\frac{1+20\alpha}{1+\alpha t},$$

in which λ refers to the wave-length *in vacuo* and α is assumed to be 0·00367. The equation is only intended to apply to small departures of temperature and pressure from 20° C and 760 mm. The results of direct calculation from this equation for air at 15 and 20° C and at 760 mm. pressure are shown in Table XII. Lastly the values directly

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calculated from our final interpolation equation (5·12) are also given. In succeeding columns of the table are given the differences between the results of the four determinations in a suitable manner for comparison.

Table XII. Comparison of results of different observers

(Values of $(n-1)\,10^6$)

Temperature and radiation		I Meggers and Peters (N.B.S.)	II Pérard (B.I.P.M.)	III Kösters and Lampe (P.T.R.)	IV Sears and Barrell (N.P.L.)	IV–I	IV–II	IV–III
15° C	λ_1	275·75	276·37	276·43	276·34	+0·59	−0·03	−0·09
	λ_2	276·44	277·12	277·20	277·12	+0·68	0·00	−0·08
	λ_3	277·11	277·85	277·94	277·86	+0·75	+0·01	−0·08
	λ_4	277·88	278·68	278·77	278·70	+0·82	+0·02	−0·07
	λ_5	278·60	279·46	279·56	279·48	+0·88	+0·02	−0·08
	λ_6	278·96	279·84	279·94	279·86	+0·90	+0·02	−0·08
	λ_7	279·64	280·57	280·66	280·58	+0·94	+0·01	−0·08
	λ_8	280·06	281·02	281·11	281·02	+0·96	0·00	−0·09
				Mean difference		+0·81	+0·01	−0·08
20° C	λ_1	271·02	271·59	271·70	271·61	+0·59	+0·02	−0·09
	λ_2	271·70	272·33	272·46	272·37	+0·67	+0·04	−0·09
	λ_3	272·35	273·04	273·19	273·10	+0·75	+0·06	−0·09
	λ_4	273·10	273·86	274·01	273·93	+0·83	+0·07	−0·08
	λ_5	273·81	274·63	274·78	274·70	+0·89	+0·07	−0·08
	λ_6	274·16	275·00	275·15	275·07	+0·91	+0·07	−0·08
	λ_7	274·82	275·72	275·86	275·78	+0·96	+0·06	−0·08
	λ_8	275·23	276·16	276·30	276·21	+0·98	+0·05	−0·09
				Mean difference		+0·82	+0·06	−0·08

The most important fact which emerges from a study of Table XII is that the Meggers and Peters' values for the visible spectrum are appreciably lower than those of the other three determinations, the difference amounting on the average to about 0·8, corresponding to nearly 1 part in 10^6 of the magnitude of the refractive index. On the whole the other three series of results are in good agreement, both for absolute values of refractive index and for dispersion, our results being on the average slightly closer to those of Pérard in absolute values, but agreeing better with those of Kösters and Lampe as to the form of the dispersion curve; furthermore, our values of refractive index are on the average intermediate between those of Pérard and Kösters and Lampe.

(*c*) *Previous N.P.L. results.* Values of the refractive index of air for the red radiation of cadmium (λ_1) have previously been obtained indirectly at the National Physical Laboratory from the optical measurements of yard and metre end-standards in terms of wave-lengths in air and *in vacuo*, and these have been published in papers dealing with the optical measurement of the fundamental standards of length. These values were derived, however, by accepting as the effective value of α at a constant pressure of about 1 atm. the value of 0·003716 determined by Pérard (1934). With the information now available from this investigation values of the refractive index of air under the conditions existing at the time of the length measurements can be calculated

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and then compared with the values actually derived from these measurements. Thus the value actually derived from the observations during the preliminary measurements of a metre end-gauge in 1931 was 1·000,267,249 in air, at 21·673° C and 753·45 mm., containing 8·7 mm. of water vapour and an assumed amount of 0·03 % of CO_2 (for which the quoted result in *Philos. Trans.* A, **231**, 126 is 1·000,276,45 for λ_1, as reduced to the conditions of dry air, at 15° C and 760 mm., containing an assumed normal proportion of CO_2). The value calculated for the observed conditions from the new interpolation equation (7·7) for atmospheric air is 1·000,267,284.

Similarly, the values of the refractive index for λ_1, actually derived from measurements of a metre and a yard end-gauge in 1933 (and quoted in *Philos. Trans.* A, **233**, 159 and 164), were 1·000,270,711 in dry, CO_2-free air at 21·005° C and 760 mm. and 1·000,270,406 in dry CO_2-free air at $21{\cdot}351_5$° C and 760 mm., for the metre and yard gauges respectively. These can now be compared with the values of 1·000,270,677 and 1·000,270,357, respectively calculated from the interpolation equation (5·12) for dry, CO_2-free air.

The observed and calculated values of $(n-1)\,10^6$ for the red radiation of cadmium are collected in Table XIII, where it will be seen that the mean value of refractivity for 1931–3, determined indirectly in the course of length measurements, differs by only $+0{\cdot}016\times10^{-6}$ from the mean value derived by calculation from the results of the investigation described in this paper.

TABLE XIII. COMPARISON OF RESULTS OBTAINED AT THE N.P.L. BETWEEN 1931 AND 1937

Date	Air conditions	Observed $(n-1)\,10^6$ for λ_1	Calculated $(n-1)\,10^6$ (1935–7)
1931	At 21·673° C and 753·45 mm., containing 8·7 mm. water vapour and assumed 0·03 % CO_2	267·249	267·284
1933	At 21·005° C and 760 mm., dry and CO_2-free	270·711	270·677
	At $21{\cdot}351_5$° C and 760 mm., dry and CO_2-free	270·406	270·357
	Mean values	269·455	269·439

(*d*) *Constancy of the refractive index of dry, CO_2-free air.* A noteworthy point arising from a careful examination of the residuals $(O-C)$ in Table VIII with respect to the dates of the various measurements is that no evidence is found for any systematic change of refractivity with sunspot activity, as has been suggested by Tilton, despite the fact that the observed values given in Table VIII were obtained at three different dates (cf. Table II) during a period of rapid increase of such activity. Another interesting feature is the remarkable constancy of the density of dry, CO_2-free air as exhibited by the refractivity measurements on forty different samples taken at different times over a period of more than a year. This property of the atmosphere at the earth's surface, after moisture and CO_2 have been removed, has been noted in our work on the optical

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measurement of length, and is at variance with the results of certain direct determinations of the density of air (Stock, Ramser and Eyber 1933), which suggest the possibility of larger variations than can be attributed from refractivity measurements.

A more stringent test of Tilton's suggestion regarding the effect of sunspot activity is made by comparing the results of the series of determinations made in August 1935, which referred to dry, CO_2-free air at 30·552° C and at eight different pressures, with those of the first part of the series of April 1937, which referred to dry, CO_2-free air at pressures near 760 mm. and at temperatures near 29·440° C. The comparison of these results is best made by reducing the 1935 values to the mean conditions corresponding to the 1937 values, using equation (5·8), for which purpose β_t may justifiably be treated as a constant for the small difference in temperature of about 1° C between the two series, while α has the theoretical value of 0·003661. It is important, for the purpose of this particular comparison, to refer only to the data obtainable from the first series (at 30·552° C), and not to make use of any information regarding the changes of refractivity with pressure and temperature which has been obtained from the whole of the first five series of determinations. The reason for this precaution is that, since the various series of observations took place in a period of about 20 months, the information obtained might itself be affected by the influence of any slight systematic changes of refractivity should such have occurred due to sunspot activity.

For a given radiation, equation (5·8) reduces to $(n_{t,p}-1) = Kp(1+\beta p)/(1+\alpha t)$. There are eight such equations for each radiation corresponding to the eight differing pressures in the August 1935 series, and from these the values of K and β for each radiation were calculated by the least squares method already described. The values thus calculated are given in the second and third columns of Table XIV; the mean value of β is $0{\cdot}75\times10^{-6}$ and it will be seen by comparison with Table IV that this is identical with the value derived from the preliminary calculation at the same temperature. Adjusted values of K to suit this mean value of β were then derived for each radiation and these are given in the fourth column of Table XIV. The values of refractivity in August 1935 corresponding to the mean temperature and pressure of the April 1937 series were then calculated by multiplying the adjusted values of K by the factor

$$p(1+0{\cdot}75\,p\times10^{-6})/(1+0{\cdot}003661t).$$

Putting $p = 760{\cdot}232$ mm. and $t = 29{\cdot}440°$ C, the value of this factor is 686·657.

The forty observed values of refractivity obtained in April 1937 are given in Table XV, together with the mean values for each radiation at the mean conditions of 29·440° C and 760·232 mm. The right-hand column of Table XV shows the changes in refractivity for each radiation over the period concerned, from which the average change for all wave-lengths is seen to be $0{\cdot}012\times10^{-6}$. This is no more than the possible experimental error of the comparison, and is similar in magnitude to that established from the internal evidence of Table VIII.

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TABLE XIV. RESULTS OF AUGUST 1935

Radiation	$K \times 10^6$ (from observations at 30·552° C)	$\beta_t \times 10^6$	$K \times 10^6$ (adjusted)	$(n-1)\,10^6$ $t = 29·440°$ C $p = 760·232$ mm.
λ_1	0·383,370	0·56	0·383,332	263·218
λ_2	0·384,242	1·09	0·384,312	263·891
λ_3	0·385,284	1·03	0·385,344	264·599
λ_4	0·386,591	0·57	0·386,545	265·424
λ_5	0·387,776	0·34	0·387,685	266·207
λ_6	0·388,290	0·34	0·388,189	266·553
λ_7	0·389,085	1·20	0·389,178	267·232
λ_8	0·389,767	0·85	0·389,782	267·647
Mean		0·75		265·596

TABLE XV. RESULTS OF APRIL 1937

Radiation	$(n-1)\,10^6$					Mean $(n-1)\,10^6$	August 1935–April 1937 $(n-1)\,10^6$
	29·446° C 760·596 mm.	29·448° C 760·009 mm.	29·438° C 760·146 mm.	29·436° C 760·164 mm.	29·432° C 760·243 mm.	29·440° C 760·232 mm.	
λ_1	263·350	3·095	3·159	3·156	3·184	263·189	+0·029
λ_2	264·008	3·795	3·877	3·878	3·907	263·893	−0·002
λ_3	264·803	4·500	4·587	4·617	4·641	264·630	−0·031
λ_4	265·603	5·332	5·412	5·416	5·432	265·439	−0·015
λ_5	266·290	6·044	6·153	6·173	6·199	266·172	+0·035
λ_6	266·663	6·422	6·495	6·504	6·513	266·519	+0·034
λ_7	267·365	7·078	7·156	7·171	7·212	267·196	+0·036
λ_8	267·796	7·504	7·606	7·624	7·668	267·640	+0·007
Mean						265·585	+0·012

Additional confirmation of the insensitivity of the refractivity of air to solar activity is provided by the good agreement of results obtained at the National Physical Laboratory in the period 1931–7 (cf. Table XIII), especially as this period approximately coincided with the transition from minimum to maximum activity.

According to Tilton (1934), the value of the refractivity for the D line in any given year can be estimated to an accuracy of $\pm 0·5 \times 10^{-6}$ from the equation

$$(n_D - 1)\,10^6 = 293·22 - 0·0148\,R,$$

where R is the relative annual sunspot number. Brunner (1937) has given the following values of relative annual sunspot numbers for recent years:

Year	R	
1933	5·7	(Minimum for present cycle)
1934	8·7	
1935	36·1	
1936	79·7	
1937	116·3	(Provisional figure, Brunner 1938)

On these bases the estimated values of $(n_D - 1)\,10^6$ according to Tilton are:

Year	$(n_D - 1)\,10^6$
1935	292·7
1936	292·0
1937	291·5

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If Tilton's suggestion were correct a change of more than 1 part in 10^6 of the value of n_D should therefore have been found between 1935 and 1937. The measured change was only about 1 part in 10^8 of the value of the mean refractive index for the visible spectrum, and within this limit it can therefore be stated that no correlation between refractivity of dry, CO_2-free air and sunspot activity has been observed.

(*e*) *Results for water vapour.* Lorenz (1880) has determined the value of the correction to be applied to the refractive index of dry air in order to obtain the refractive index of moist air. If f is the vapour pressure in mm., then, according to Lorenz, the correction for all colours is $-0{\cdot}000{,}041 f/760$, which corresponds to a uniform correction in the visible spectrum of $-0{\cdot}054\times10^{-6}$ per mm. of water vapour. This may be compared with the value of $-0{\cdot}0556\times10^{-6}$ per mm. which has been calculated from the results of our investigations on moist air in § 7 (*c*).

The only recorded determination of the dispersion of water vapour that we have noticed is that due to C. and M. Cuthbertson (1914), and their results for steam are expressed in the form of a Sellmeier equation thus:

$$(n_0'-1) = 2{\cdot}62707\times10^{27}/(10697\times10^{27}-\nu^2),$$

where $(n_0'-1)$ is the refractivity at 0° C and 760 mm. In deriving this expression, relating to the conditions 0° C and 760 mm., from the results of observations on water vapour under actual experimental conditions, C. and M. Cuthbertson have made allowances for the departures of the vapour from the Avogadro-Ampère law, so that their results may be compared with those obtained from our investigation of the refraction and dispersion of water vapour.

The Sellmeier equation above, when converted to a two-term Cauchy equation, becomes

$$(n_0'-1)\,10^6 = 245{\cdot}40+2{\cdot}187\,\lambda^{-2}, \qquad (8{\cdot}1)$$

where λ is the wave-length *in vacuo*. The interpolation equation (7·3) determined from our experiments with water vapour is

$$(n_{t,f}'-1)10^6 = \left[0{\cdot}3159+\frac{0{\cdot}002963}{\lambda^2}\right]\frac{f(1+\beta_t' f)}{1+0{\cdot}003661\,t}.$$

If we put $t = 0°$ C, $f = 760$ mm. and $\beta_0' = 32{\cdot}9\times10^{-6}$ per mm., as calculated from the critical constants of water vapour by equation (6·15), assuming $\beta_0' = -\delta_0$, then

$$(n_0'-1)\,10^6 = 246{\cdot}09+2{\cdot}308\,\lambda^{-2}. \qquad (8{\cdot}2)$$

The values of $(n_0'-1)\,10^6$, for the eight radiations mentioned in Table I, calculated from equations (8·1) and (8·2) are compared below in Table XVI.

The agreement both for refractivity and dispersion is within the limits of reasonable expectations, taking into account that neither equation is considered to have a greater accuracy than ±1 part in 500. Assuming an average vapour pressure of 10 mm. in

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atmospheric air, the corrections of refractivity to the dry air condition as derived from equations (8·1) and (8·2) differ by less than $0{\cdot}02 \times 10^{-6}$.

TABLE XVI. COMPARISON OF RESULTS FOR WATER VAPOUR

Radiation	$(n_0' - 1)\,10^6$ C. and M. Cuthbertson I	N.P.L. II	Differences II–I
λ_1	250·7	251·6	+0·9
λ_2	251·7	252·8	+1·1
λ_3	252·7	253·8	+1·1
λ_4	253·8	255·0	+1·2
λ_5	254·9	256·1	+1·2
λ_6	255·4	256·6	+1·2
λ_7	256·3	257·6	+1·3
λ_8	256·9	258·2	+1·3
		Mean difference	+1·2

(*f*) *Optical determinations of β*. Opladen (1927) has collected a series of values of β determined by different observers from refractivity measurements on air over different ranges of pressure, and as a matter of interest they are quoted in Table XVII for comparison with the value that has been determined from this investigation. They are arranged in two sections according to the pressure range over which the values have been determined; the temperatures to which the determinations refer are also included, although in two results it has not been possible to ascertain these from the original publications.

TABLE XVII. VALUES OF $\beta \times 10^6$ DETERMINED BY DIFFERENT OBSERVERS FROM REFRACTIVITY MEASUREMENTS ON AIR

Over 1 atm.			Under 1 atm.		
Observers	Temp. (° C)	$\beta \times 10^6$	Observers	Temp. (° C)	$\beta \times 10^6$
Mascart (1877)	22	0·72	Kaiser (1904)	—	0·95
Chappuis and Rivière (1888)	21	0·58	Posejpal (1917)	16	3·57
Perreau (1896)	16	0·90	Unterbusch (1924)	—	1·57
Opladen (1927)	17·5	0·52	Pérard (1934)	0–100	2·40
			Zwetsch (1923)	0	6·67
Mean value	19	0·68	Sears and Barrell (1938)	21	0·72

As we have already mentioned, in § 6 (*d*), the determination of β from refractivity measurements demands extremely high precision in the work. We believe that the high values recorded by other observers for the lower pressure range are probably due to the insufficient accuracy of their measurements to afford reliable values of β. Our value is appreciably lower than any which has so far been determined within the lower pressure range, but is in fairly close agreement with the mean value determined at

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higher pressures, where a higher experimental accuracy of determination of β is naturally attainable. Thus, no evidence has been found in favour of Posejpal's suggestion (1921) that β varies inversely with pressure for values of the latter below 4 atm.

(*g*) *Temperature coefficient of refractivity*. The preliminary reduction of the results of refractivity yielded a value of $\alpha = 0{\cdot}003674$ per 1° C. A very similar result can be derived from the final interpolation equation (5·12) by employing it to calculate the refractivities of air at 760 mm. pressure and at temperatures of 12 and 31° C, which are closely the limiting temperatures of the range investigated. If the values of refractivity thus calculated are denoted by (n_1-1) and (n_2-1) respectively, then the mean value of the temperature coefficient at a constant pressure of 1 atm. which is effective over the range 12–31° C can be calculated from the expression

$$(n_1-1)\,(1+12\alpha) = (n_2-1)\,(1+31\alpha).$$

Since $(n_1-1)\,10^6$ for $\lambda_1 = 279{\cdot}255$ and $(n_2-1)\,10^6$ for $\lambda_1 = 261{\cdot}750$, this leads to a value of $\alpha = 0{\cdot}003675$. From the determinations made by Chappuis (1907) with the constant pressure gas thermometer, filled either with air or nitrogen, the value of the temperature coefficient of expansion between 0 and 40° C, and at 760 mm. pressure, is found to be 0·003672. The same value may also be derived from the 0 and 50° C isothermals for air at 760 mm. pressure determined by Holborn and Schultze (1915).

It was mentioned in the introduction that previous determinations of the temperature coefficient of refractivity have yielded values ranging from 0·00311 to 0·00382. Among recent determinations, that of Meggers and Peters gave a value of the coefficient between 0 and 30° C which varies with wave-length, the average value for the visible spectrum being 0·003694, whereas that of Pérard gave a value of 0·003716 for the range of temperature from 0 to 100° C. As with determinations of β, small variations in the magnitude and distribution of experimental errors in the refractivity measurements may lead to relatively large variations in the derived value of the temperature coefficient. We consider that the high values of temperature coefficient obtained by Meggers and Peters and by Pérard may be due to this cause. If we accept as a criterion of the accuracy attained by a particular observer (or observers) the probable magnitude of the difference between a single observed value of refractive index and the value obtained from an interpolation equation derived from all the observations, then the accuracy achieved by Meggers and Peters is $\pm 0{\cdot}33\times 10^{-6}$, and by Pérard is $\pm 0{\cdot}20\times 10^{-6}$, compared with $\pm 0{\cdot}01_5\times 10^{-6}$ which has been computed for the present investigation in the discussion based on Table VIII in § 5 (*c*). The present investigation leads to the closest agreement between the values of the coefficient of expansion of air at constant pressure determined from refractivity measurements and from the gas thermometer.

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10. SUMMARY

The refraction and dispersion of dry, CO_2-free air in the visible spectrum has been investigated, at temperatures between 12 and 31° C and at pressures between 100 and 800 mm. of mercury, by means of an interference refractometer which employs Brewster's fringes produced by two 67 cm. Fabry-Perot étalons. The results are used to provide a general interpolation equation from which definitive values of the refractive index may be calculated; the magnitude of the probable difference between a single observed value of refractive index and the value calculated from the equation is $\pm 0{\cdot}01_5 \times 10^{-6}$. The form of this equation, being derived from considerations based on the Lorenz-Lorentz relation between refractive index and density of transparent media and on D. Berthelot's representation of the characteristic behaviour of gases at low pressures, enables interesting comparisons to be made between the results of refractivity and compressibility measurements on air regarding the departure of the gas from Avogadro's law.

The effect of humidity on the refraction of atmospheric air has been determined from refractivity measurements on moist, CO_2-free air containing known amounts of unsaturated vapour.

No evidence has been found in favour of Tilton's suggested relationship between the refractivity of air and sunspot activity.

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