

# Optical Refractive Index of Air: Dependence on Pressure, Temperature and Composition

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The theoretical background and present status of formulas for the refractive index of air are reviewed. In supplement to Edlén's recently revised formula for relative refractivity, the density dependence of refractive index is reanalyzed. New formulas are presented for both phase and group refractive index which are more useful over a wide range of pressure, temperature, and composition than any presently available. The application of the new formulas to optical distance measuring is briefly discussed.

## I. Introduction

Spectroscopic and metrological measurements are always made in air if possible, but accurate work requires conversion of the directly observed wavelength,  $\lambda_{\text{air}}$ , into the corresponding wavelength in vacuum,  $\lambda_{\text{vac}} = n\lambda_{\text{air}}$ . In order to make this conversion with maximum accuracy the refractive index  $n$  must be known at least as well as the precision to which the present wavelength standard is defined,  $1 \times 10^{-8}$ . In practice it is difficult to control the composition of the air in an optical instrument sufficiently well to achieve this accuracy, and recommended metrological practice requires the actual measurement of the refractive index of the air in the optical path.<sup>1</sup> Accurate formulas for the refractivity ( $n - 1$ ) of air as a function of pressure, temperature, humidity and wavelength are still required, however. In such low-precision applications of laser interferometry as machine tool control it is adequate simply to use formulas rather than to measure ( $n - 1$ ) directly. In addition, methods for the optical measurement of length through the uncontrolled atmosphere using simultaneous measurements at two or more wavelengths have recently been described<sup>2,3</sup> which require accurate formulas for relative refractivity as a function of air composition.

Edlén has recently reviewed the measurements made since 1953 and has suggested a revision<sup>4</sup> of his earlier dispersion formula<sup>5</sup> for air. Although he estimates that the ratio of refractive indices at different wavelengths for dry air as given by the new formula is accurate to better than  $1 \times 10^{-9}$ , discrepancies among the few available absolute measurements indicate

that the absolute accuracy of the formula may not be better than  $5 \times 10^{-8}$ . The additional uncertainty due to water vapor in uncontrolled air may be even larger because the absolute measurements of Barrell and Sears<sup>6</sup> on which Edlén's results for moist air are based were made over a limited range of conditions. Although the wavelength dependence given by the new formula could be improved only by new measurements, and the range of pressures and temperatures for which it is applicable is more than adequate for laboratory use, this range does not cover all conditions that may be encountered in atmospheric work. Therefore, the density dependence of the refractive index of air has been reanalyzed, and new formulas are presented for phase and group refractive index that are useful over a wider range of pressure, temperature, and composition. In this analysis the parameters of a suitably general equation of state were determined for each of the important constituents of air by least-squares polynomial computer curve fitting to recently reported thermodynamic data. The curve fitting was performed sufficiently accurately so the resulting expressions for the densities of dry, CO<sub>2</sub>-free air, water vapor, and carbon dioxide could be used to predict refractivity, assuming the validity of the Lorenz—Lorentz equation, to an accuracy of  $3 \times 10^{-6}$  relative to standard conditions (corresponding to  $1 \times 10^{-9}$  in  $n$ ) over the ranges 0–4 atm total pressure, 250°K to 320°K, 0–100% relative humidity, and 0–17 mb CO<sub>2</sub> partial pressure.

## II. Theoretical Background

The quantum theory of atomic and molecular polarizability and the classical electromagnetic theory relating this polarizability to refractive index have long been well understood, although a satisfactory many-body treatment of the local field problem has not yet been given. A thorough review of the classical theory has been given by Böttcher.<sup>7</sup> It may be shown

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from the Lorenz-Lorentz equation that the refractive index of a mixture of nonpolar gases is given by the relation

$$\frac{n^2 - 1}{n^2 + 2} = \sum_i R_i \rho_i, \quad (1)$$

in which  $R_i$  is the specific refraction and  $\rho_i$  the partial density of the  $i$ th component of the mixture. The specific refraction, which is invariant under changes in density to a high degree of approximation for the components of air at atmospheric pressures and hence may be evaluated from absolute measurements of refractivity vs wavelength at one density, is given by

$$R_i = [(n_i^2 - 1)/(n_i^2 + 2)](1/\rho_i) \quad (2)$$

$$= \frac{4}{3} \pi (N_A/M_i) \alpha_i, \quad (3)$$

in which  $n_i$ ,  $M_i$ , and  $\alpha_i$  are the refractive index at density  $\rho_i$ , the molecular weight, and the polarizability, respectively, of the  $i$ th component, and  $N_A$  is Avogadro's number.

The use of Eq. (1) to represent the refractive index of a gas mixture, in which the contribution of each component is given by the product of the partial density and a quantity  $R_i$  which depends only on wavelength, assumes that the Lorentz local field is correct and that the polarizabilities of the components are unchanged in the mixture. Neither of these assumptions is strictly true. Böttcher has pointed out that the Lorentz field gives only the volume average of the local field rather than the time-averaged field at the individual particles, and that the local field is, in fact, different for the different kinds of molecules in the mixture. A better approximation for the local field which he suggests leads to a different definition of the invariant quantity, specific refraction. It may be shown from this formula that the specific refraction of dry air as defined by Eq. (2) should not, in fact, be completely invariant, but should increase by about 0.01% for an increase in pressure of 0.5 atm. This result has been verified only qualitatively, however, and because it is also based on a cavity definition of the local field it may not fully compensate for the known deficiencies of the Lorentz formula. Until definitive absolute measurements of refractivity as a function of density are carried out it seems preferable to use the definition in Eq. (2) of specific refraction rather than Böttcher's definition.

For atmospheric air it is sufficient to write Eq. (1) as the sum of three terms,

$$(n^2 - 1)/(n^2 + 2) = R_1 \rho_1 + R_2 \rho_2 + R_3 \rho_3, \quad (4)$$

in which  $R_1$ ,  $R_2$ , and  $R_3$  are the specific refractions of dry, CO<sub>2</sub>-free air, of water vapor, and of carbon dioxide, respectively, and  $\rho_1$ ,  $\rho_2$ , and  $\rho_3$  are the corresponding partial densities. The dispersion curves of N<sub>2</sub>, O<sub>2</sub>, and Ar are sufficiently similar that all three may be represented by the first term. In addition, the measurements on which the present analysis is based were made on dry air rather than on its individual components.

### III. Evaluation

#### A. Dry CO<sub>2</sub>-free Air

Standard air is defined to be dry air at a temperature of 15°C and a total pressure of 1013.25 mb, having the following composition by molar percentage: 78.09 N<sub>2</sub>, 20.95 O<sub>2</sub>, 0.93 Ar, and 0.03 CO<sub>2</sub>. The refractivity of dry, CO<sub>2</sub>-free air of otherwise standard composition required for the evaluation of  $R_1$  was found by dividing Edlén's 1966 dispersion formula for standard air by 1.000162 to remove the effect of carbon dioxide, giving

$$(n - 1) \times 10^8 = 8340.78 + [2,405,640/(130 - \sigma^2)] + [15,994/(38.9 - \sigma^2)], \quad (5)$$

in which  $\sigma = 1/\lambda_{\text{vac}}$  is the vacuum wavenumber. It may be shown from the dispersion formula of Koch<sup>8</sup> that the error introduced by using the number 1.000162 in the conversion from standard air to CO<sub>2</sub>-free air, neglecting the actual dispersion of CO<sub>2</sub>, is only  $3 \times 10^{-10}$  over the range 3650–6328 Å.

The data used for the derivation of the new density expression were the tabulated values of compressibility factor  $Z = PV/RT$  given by Hilsenrath<sup>9</sup>, from which the density may be found by using the relation

$$\rho = (MP/RT)(1/Z), \quad (6)$$

in which  $M$  is the average molecular weight and  $P$ ,  $R$ , and  $T$  have the usual meaning. The inverse compressibility factor was represented by

$$1/Z = 1 + P\beta(P)\gamma(T), \quad (7)$$

and values of the function

$$\begin{aligned} \delta(P, T) &= [(1/Z) - 1]/P \\ &= \beta(P)\gamma(T) \end{aligned} \quad (8)$$

were calculated. As a first step, the function  $\beta(P)$  was estimated by plotting  $\delta(P, T)$  vs  $P$  for several values of  $T$ , and it was found that  $\beta(P)$  could be set equal to one at this stage for pressures below 4 atm. Discrepancies occurring below 0.1 atm and near 0.7 atm could be attributed to rounding errors in the tables and were not believed to be significant. Next, values of  $\delta(T)$ , which are shown in Fig. 1, were obtained by averaging the values of  $\delta(P, T)$  corresponding to pressures of 0.4 atm, 0.7 atm, 1.0 atm, and 4.0 atm. The spread of  $\delta(P, T)$  values around the average is less than  $2 \times 10^{-5}$  at any temperature considered. These values of  $\delta(T)$  were plotted against  $T$  in various ways in order to find the simplest functional form for  $\gamma(T)$ . It was found that the best two-parameter fit was given by  $\gamma(T) = a + b/T^3$ , but that the simplest satisfactory fit was given by  $\gamma(T) = a + b/T + c/T^2$ . Least-squares curve fitting by computer was then carried out, and the parameters  $a$ ,  $b$ , and  $c$  obtained. It was found that a quadratic function would, in fact, give adequate accuracy, and that polynomials of higher order provided little improvement. Finally, values of the function  $\delta(P, T)/\gamma(T) = \beta(P)$  were calculated, and it was found that the earlier result,  $\beta(P) = 1$ , did not require revision. Representative values illustrating the scatter of these points are shown in

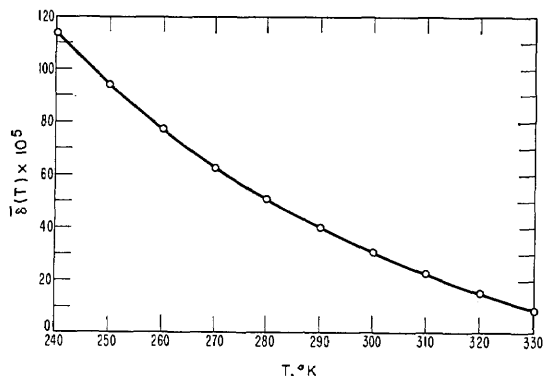


Fig. 1. Mean temperature dependence of deviation from ideal gas behavior for dry air, 0.4–4.0 atm.

Fig. 2. Having thus found a satisfactory expression for  $1/Z$ , the constant  $M/R$  in Eq. (6) was evaluated using the density of standard air at  $0^\circ\text{C}$  as given by Hilsenrath. The density of  $\text{CO}_2$ -free air was obtained by multiplying by 0.99984, the ratio of the average molecular weights of  $\text{CO}_2$ -free and standard air. The resulting expression for the density of dry,  $\text{CO}_2$ -free air of otherwise standard composition is

$$\rho(\text{g/m}^3) = 348.328 \frac{P}{T} \left[ 1 + P \left( 57.90 \times 10^{-8} - \frac{0.94581 \times 10^{-3}}{T} + \frac{0.25844}{T^2} \right) \right], \quad (9)$$

in which  $P$  is in millibars and  $T$  is in  $^\circ\text{K}$ .

The refractive index of dry,  $\text{CO}_2$ -free air under non-standard conditions or the contribution of this component to the refractive index of moist air may now be found using Eq. (4). The specific refraction of Eq. (2) is evaluated using Eq. (5) for the refractivity under standard conditions and the corresponding density, which is in turn found from Eq. (9) by using  $P = 1013.25$  mb and  $T = 288.16^\circ\text{K}$ . The density  $\rho_1$  for the conditions of interest is given directly by Eq. (9).

Although the compressibility factors tabulated by Hilsenrath are given to a precision of only  $1 \times 10^{-5}$  and some of the experimental data used in the compilation deviate by considerably more than this, it is be-

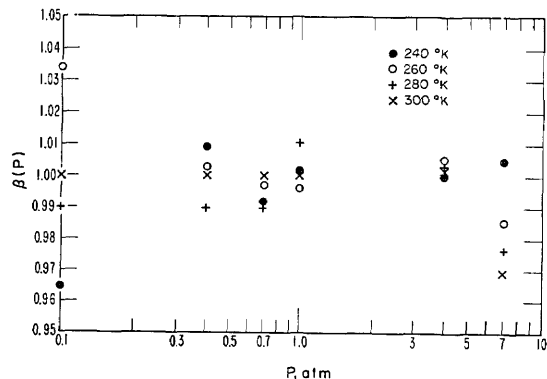


Fig. 2. Pressure dependence of deviation from ideal gas behavior at various temperatures for dry air.

lieved that averaging of the tabulated values over the range of conditions considered here may increase their reliability by smoothing out rounding errors. The uncertainties in density resulting from an imperfect fit of Eq. (9) to the averaged tabulated values are not greater than  $3 \times 10^{-6}$  over the range 0–4 atm and  $240^\circ\text{K}$  to  $330^\circ\text{K}$ . The improvement in density, and hence in refractivity, obtainable through the use of the new Eq. (9) may be seen by a direct comparison with Edlén's recent work. By combining Eqs. (6) and (7) we may write

$$\rho = C(P/T)[1 + P\beta(P)\gamma(T)] \quad (10)$$

in which  $C$  is a constant. The error in density due to an error in the correction factor  $P\beta\gamma$  is given by

$$\Delta\rho = C \frac{P}{T} \Delta[P\beta(P)\gamma(T)]. \quad (11)$$

Expressing this as an error relative to the density  $\rho'$  at a pressure of 1 atm but at the same temperature and neglecting  $P\beta\gamma$  in the denominator, we have

$$(\Delta\rho/\rho') = P\Delta[P\beta(P)\gamma(T)]. \quad (12)$$

The errors in relative density given by Eq. (12) owing to discrepancies between the values of  $P\beta\gamma$  derived from Hilsenrath's tables and those calculated from Edlén's formula and from the new expression for density are given in Table I. It may be seen that the

Table I. Comparison of Density Formulas

Gas	Conditions	Density error due to deviations from thermodynamic data	
		New formula	Edlén
Dry air	250°K, 1 atm	$-1.4 \times 10^{-6}$	$-145.0 \times 10^{-6}$
	280°K, 1 atm	$0.0 \times 10^{-6}$	$-1.7 \times 10^{-6}$
	300°K, 1 atm	$+1.0 \times 10^{-6}$	$+3.2 \times 10^{-6}$
	320°K, 1 atm	$-0.9 \times 10^{-6}$	$-44.4 \times 10^{-6}$
Water vapor	250°K, 0.0004 atm	$-3.6 \times 10^{-12}$	$-2.1 \times 10^{-8}$
	280°K, 0.006 atm	$-6.6 \times 10^{-9}$	$-1.8 \times 10^{-6}$
	300°K, 0.021 atm	$-5.1 \times 10^{-8}$	$-1.1 \times 10^{-5}$
	320°K, 0.06 atm	$-4.6 \times 10^{-7}$	$-4.3 \times 10^{-5}$

new Eq. (9) is in error by not more than  $1.5 \times 10^{-6}$  over the full range of temperature considered. Although Edlén's simpler formula is significantly less accurate at the ends of the range, over the region 5–30°C for which it was derived it gives results accurate to about  $3 \times 10^{-6}$ , which is adequate to give  $n$  to  $1 \times 10^{-9}$ .

## B. Water Vapor

The refractivity of water vapor, the most important of the variable constituents of atmospheric air, is found under known conditions by multiplying Erickson's<sup>10</sup> accurate formula for relative refractivity by  $307.01 \times 10^{-8}$ , the value of refractivity given by Barrell and Sears' absolute measurements at 4679.46 Å, 10 torr (13.33 mb), and 20°C. The resulting equation for the absolute refractivity of water vapor under these conditions of temperature and pressure is

$$(n - 1) \times 10^8 = 295.235 + 2.6422\sigma^2 - 0.032380\sigma^4 + 0.004028\sigma^6. \quad (13)$$

The derivation of a formula for density is carried out in the same way as for dry air. However, the compressibility factor of saturated water vapor at low temperature has apparently not been tabulated, and it was necessary to use values calculated from the equation of state of Goff and Gratch:<sup>11</sup>

$$PV = RT - A_{ww}P - A_{www}P^2. \quad (14)$$

The virial coefficients  $A_{ww}$  and  $A_{www}$  are given by the following empirical relations, in which  $\tau = 1/t$  and  $t$  is temperature in degrees Rankine:

$$A_{ww} = -0.0302 + 88.514\tau^{10}233280\tau^2 \\ A_{www} = 67.4\tau^2A_{ww}^3. \quad (15)$$

The compressibility factor given by Eq. (14) may be written as

$$Z = 1 - 13.7066 A_{ww}(P/T) - (2.90063 \times 10^4)A_{www}(P^2/T), \quad (16)$$

in which the virial coefficients are to be evaluated using degrees Rankine as given by Eq. (15), but  $P$  and  $T$  are in atmospheres and degrees Kelvin, respectively. At a given temperature, only water vapor pressures less than or equal to the saturation pressure  $P_s(T)$  were used in the evaluation of  $Z$ . The best available formula for  $P_s(T)$  has recently been given by Goff:<sup>12</sup>

$$\log_{10}(P_s/P_0) = 10.79586(1 - T_0/T) - 5.02808 \log_{10}(T/T_0) \\ + 1.50474 \times 10^{-4}[1 - 10^{-8.29692(T/T_0 - 1)}] \\ + 0.42873 \times 10^{-3}[10^{4.76955(1 - T_0/T)} - 1] \\ - 2.2195983. \quad (17)$$

In this formula,  $P_s$  is the saturation vapor pressure in millibars of pure water vapor in equilibrium with a plane water surface,  $P_0$  is standard atmospheric pressure (1013.25 mb), and  $T_0$  is 273.16°K. For measurements of highest accuracy it must be noted that the saturation pressure of pure water vapor at a given temperature is not the same as the saturation pressure

Table II. Saturation Pressure and Deviations from Ideal Gas Behavior of Water Vapor

$T, ^\circ\text{K}$	$P_s(T), (10^{-3} \text{ atm})$	$\bar{\delta}(T) \times 10^2$
240	0.270	20.674
250	0.751	15.180
260	1.933	11.469
270	4.633	8.8807
280	9.774	7.0268
290	18.917	5.6652
300	34.844	4.6393
310	61.382	3.8538
320	103.88	3.2455
330	169.56	2.7656

of water vapor in moist air. The latter depends upon the total pressure of the moist air as well as the temperature, and the two saturation pressures differ by about 0.5% at 1 atm and 20°C. A discussion of this effect has been given by Harrison.<sup>13</sup>

In the first step of curve fitting, values of  $\delta(P, T)$  were calculated for the range 240°K to 330°K and pressures from zero to saturation at each temperature. The temperature dependence of  $\delta(P, T)$  was again found to be much stronger than the pressure dependence, and so an average value  $\bar{\delta}(T)$  was calculated at each temperature by averaging over pressure. These average values, as well as the saturation pressures in atmospheres, are given in Table II. A polynomial in  $1/T$  fitted to the  $\bar{\delta}(T)$  values was used as a first approximation to  $\gamma(T)$ , and the function  $\beta(P) = \delta(P, T)/\gamma(T)$  was calculated. It was found that the simple relation  $\beta(P) = 1 + 0.37 P$  was satisfactory. This choice necessitated the renormalization of  $\gamma(T)$ , which was recalculated and refit by a new polynomial. The final result, after conversion of the pressure units to millibars and evaluation of the constant giving absolute density, is

$$\rho(\text{g/m}^3) = 216.582(P/T)[1 + P\beta(P)\gamma(T)], \quad (18)$$

in which

$$\beta(P) = 1 + (3.7 \times 10^{-4})P \\ \gamma(T) = -2.37321 \times 10^{-3} + \frac{2.23366}{T} - \frac{710.792}{T^2} \\ + \frac{7.75141 \times 10^4}{T^3}.$$

This expression gives values of density deviating by less than  $1 \times 10^{-6}$  relative to 1 atm from the Goff and Gratch values for the range 250°K to 320°K and 0–100 mb. Its absolute accuracy is difficult to estimate, but probably is not worse than a few parts in  $10^6$  relative to 1 atm, according to the discussion given by Goff and Gratch. The comparison of Eq. (18) and Edlén's expression for water vapor density given by Eq. (12) at 50% R.H. is presented in Table I. Edlén's excellent agreement with the new data, the error being only  $11 \times 10^{-6}$  at 300°K and 0.021 atm, is surprising in view of the fact that his formula is based on Barrell and Sears' limited optical measurements using moist air

rather than on thermodynamic data. Considering the limited accuracy of the classical psychrometric and dew-point methods of humidity measurement,<sup>14</sup> Edlén's formula is more than satisfactory, and the new Eq. (18) will be required only under conditions of high temperature and humidity when the most accurate methods of humidity measurement are used.

## C. Carbon Dioxide

Although the effects of carbon dioxide are usually small, there are situations in which an abnormally high CO<sub>2</sub> content could cause noticeable errors, and therefore it is treated separately. The best available dispersion formula is given by Edlén for 15°C and 1013.25 mb:

$$(n - 1) \times 10^8 = 22,822.1 + 117.8\sigma^2 + \frac{2,406,030}{(130 - \sigma^2)} + \frac{15,997}{(38.9 - \sigma^2)}. \quad (19)$$

The partial density of CO<sub>2</sub> is always so small that ideal gas behavior may be assumed. This gas deviates relatively strongly from ideal behavior at 1 atm, however, and therefore the constant required for the conversion of relative to absolute density was obtained by using Hilsenrath's tabulated value of  $\rho/\rho_0$  at 0.01 atm rather than at 1 atm. The density of CO<sub>2</sub> at low pressures may then be written

$$\rho(\text{g/m}^3) = 529.37(P/T). \quad (20)$$

This equation gives the density to an accuracy of  $1 \times 10^{-6}$  relative to 1 atm over a much wider range than necessary; for a pressure of 0.01 atm, thirty times the normal concentration, it is valid for any  $T > 200^\circ\text{K}$ .

The formulas derived in the preceding sections are collected for convenient reference in Table III, in which the absolute values of refractive index, refractivity, and density under one set of conditions required for the calculation of the specific refraction of the  $i$ th component are denoted by  $(n_0)_i$ ,  $r_i = [(n_0)_i - 1]$ , and  $(\rho_0)_i$ , respectively, and the subscripts  $i = 1, 2, 3$  refer to dry, CO<sub>2</sub>-free air, water vapor, and carbon dioxide, in that order. The ranges of wavelength over which dispersion measurements have been made and the ranges of pressure and temperature over which the new density expressions may be expected to give values of  $n$  accurate to  $1 \times 10^{-9}$ , assuming the validity of the Lorenz-Lorentz equation, are also given. It should be emphasized again that, if Böttcher is correct, the error in  $n$  introduced by this assumption of the Lorentz local field may be as great as  $3 \times 10^{-8}$  at a pressure differing from standard conditions by 0.5 atm.

## D. Simplified Formula

A simpler formula that retains most of the advantages of the more accurate density factors may be obtained by making the approximation

$$(n^2 - 1)/(n^2 + 2) = (n - 1)[1 - (n - 1)/6]_2^2. \quad (21)$$

This permits Eq. (1) to be rewritten as

Table III. Summary of Formulas

### I. General formulas

$$\frac{n^2 - 1}{n^2 + 2} = \sum_{i=1}^3 R_i \rho_i$$

$$R_i = \frac{(n_0)_i^2 - 1}{(n_0)_i^2 + 2} \frac{1}{(\rho_0)_i}$$

### II. Dry, CO<sub>2</sub>-free air

$$r_1 \times 10^8 = 8340.78 + \frac{2,405,640}{(130 - \sigma^2)} + \frac{15,994}{(38.9 - \sigma^2)}$$

$$\rho_1 = 348.328 \frac{P_1}{T} \left[ 1 + P_1 \left( 57.90 \times 10^{-8} - \frac{9.4581 \times 10^{-4}}{T} + \frac{0.25844}{T^2} \right) \right]$$

$$(\rho_0)_1 = \rho_1(P = 1013.25 \text{ mb}, T = 288.16^\circ\text{K})$$

Range of validity: 2302–20,586 Å

$$240^\circ\text{K} < T < 330^\circ\text{K}$$

$$0 < P < 4 \text{ atm}$$

### III. Water vapor

$$r_2 \times 10^8 = 295.235 + 2.6422\sigma^2 - 0.032380\sigma^4 + 0.004028\sigma^6$$

$$\rho_2 = 216.582 \frac{P_2}{T} \left\{ 1 + P_2 \left[ 1 + \left( 3.7 \times 10^{-4} \right) P_2 \right] \times \left[ -2.37321 \times 10^{-3} + \frac{2.23366}{T} - \frac{710.792}{T^2} + \frac{7.75141 \times 10^4}{T^3} \right] \right\}$$

$$(\rho_0)_2 = \rho_2(P = 13.33 \text{ mb}, T = 293.16^\circ\text{K})$$

Range of validity: 3611–6440 Å

$$250^\circ\text{K} < T < 320^\circ\text{K}$$

$$0 < P < 100 \text{ mb}$$

### IV. Carbon dioxide

$$r_3 \times 10^8 = 22,822.1 + 117.8\sigma^2 + \frac{2,406,030}{(130 - \sigma^2)} + \frac{15,997}{(38.9 - \sigma^2)}$$

$$\rho_3 = 529.37 \frac{P_3}{T}$$

$$(\rho_0)_3 = \rho_3(P = 1013.25 \text{ mb}, T = 288.16^\circ\text{K})$$

Range of validity: 2379–6910 Å

$$240^\circ\text{K} < T < 330^\circ\text{K}$$

$$0 < P < 17 \text{ mb}$$

$$n - 1 = \sum_i R_i' \rho_i', \quad (22)$$

in which the modified specific refraction  $R_i'$  and the modified density  $\rho_i'$  are given by

$$R_i' = (n_i - 1)[1 - (n_i - 1)/6](1/\rho_i) \quad (23)$$

and

$$\rho_i' = \rho_i/[1 - (n - 1)/6]. \quad (24)$$

It is adequate for the evaluation of  $R_i'$  and  $\rho_i'$  to neglect the dispersion of the bracketed factors, using average values  $\langle n_i - 1 \rangle$  and  $\langle n - 1 \rangle$  for the visible spectrum. The modified density may then be written, using the equation of state (7), as

$$\rho_i' = C_i(P_i/T)[1 + P_i\beta_i(P_i)\gamma_i(T)]/(1 - \langle n - 1 \rangle/6). \quad (25)$$

Because the factor  $\langle n - 1 \rangle/6$  is small, it is sufficient to use

$$\langle n - 1 \rangle \approx \langle R_1' \rangle C_1(P_1/T), \quad (26)$$

in which  $\langle R_1' \rangle$  is the average value corresponding to  $\langle n - 1 \rangle$ . Defining a new constant by  $D_1 = \langle R_1' \rangle C_1/6$  and dropping small terms, we may rewrite Eq. (25) for dry air as

$$\rho_1' = C_1(P_1/T)[1 + P_1(\beta_1\gamma_1 - D_1/T)], \quad (27)$$

and hence the first term of the sum in Eq. (22) is given by  $f_1\nu_1\rho_1'$ , in which  $f_1$  is defined by

$$f_1 = [1 - \langle n_1 - 1 \rangle_0/6]/(\rho_0)_1. \quad (28)$$

The subscript 0 means as before that these terms are to be evaluated under some standard conditions. In order to simplify the formula further, the dispersion factor was adjusted to include the effects of 0.03% CO<sub>2</sub>; hence the subscript  $s$  rather than 1 will be used to indicate that air of standard composition is meant. In finding the contribution made by water vapor, the same steps were carried out, except that the average refractivity of dry air at 1 atm and 15°C was used in the denominator of Eq. (25) rather than including the pressure and temperature dependence as in Eq. (26). In the equation for  $f_2$  analogous to Eq. (28), however,  $\langle n_2 - 1 \rangle_0$  was used.

The simplified formula which finally results for the refractivity of moist air having partial pressures  $P_s$  and  $P_w$  of dry air containing 0.03% CO<sub>2</sub> and of water vapor, respectively, is

$$(n - 1) \times 10^8 = \left[ 2371.34 + \frac{683,939.7}{(130 - \sigma^2)} + \frac{4547.3}{(38.9 - \sigma^2)} \right] D_s + [6487.31 + 58.058\sigma^2 - 0.71150\sigma^4 + 0.08851\sigma^6] D_w, \quad (29)$$

where the density factors  $D_s$  and  $D_w$  for dry air and water vapor are given by

$$D_s = \frac{P_s}{T} \left[ 1 + P_s \left( 57.90 \times 10^{-8} - \frac{9.3250 \times 10^{-4}}{T} + \frac{0.25844}{T^2} \right) \right] \quad (30)$$

and

$$D_w = \frac{P_w}{T} \left\{ 1 + P_w \left[ 1 + \left( 3.7 \times 10^{-4} \right) P_w \right] \left[ -2.37321 \times 10^{-3} + \frac{2.23366}{T} - \frac{710.792}{T^2} + \frac{7.75141 \times 10^4}{T^3} \right] \right\}. \quad (31)$$

A comparison of the refractivities calculated using Edlén's formula, the new expression summarized in Table III, and the simplified Eq. (29) is given in Table IV. For this comparison Edlén's intermediate results were combined to yield the general expression

$$(n - 1) \times 10^8 = \left[ 8342.13 + \frac{2,406,030}{(130 - \sigma^2)} + \frac{15,997}{(38.9 - \sigma^2)} \right] \times \left( \frac{p}{720.775} \right) \left[ \frac{1 + p(0.817 - 0.0133t) \times 10^{-6}}{1 + 0.0036610t} \right] - f[5.722 - 0.0457\sigma^2], \quad (32)$$

in which  $p$  is the total pressure in torricelli,  $f$  is the partial pressure of water vapor in torricelli, and  $t$  is the temperature in degrees centigrade. It may be seen from Table IV that the pressure dependence of refractivity given by Edlén's formula is good, although the temperature dependence is less accurate. The most serious discrepancies occur, as expected, under conditions of high temperature and high humidity, where the values calculated from Eq. (32) differ from those obtained using the new formulas by as much as  $39.1 \times 10^{-8}$  at 1000 mb, 45°C, and 100% R.H.

#### IV. Group Refractive Index

For applications in which modulated light is used, the group velocity  $U$  rather than the phase velocity is required. We may define the group refractive index  $n^G$  by

$$n^G = (c/U) \quad (33)$$

in which  $c$  is the velocity of light in vacuum. The group refractive index is related to the ordinary refractive index  $n$  by<sup>15</sup>

$$n^G = n + \sigma(dn/d\sigma). \quad (34)$$

For numerical evaluation, it is more satisfactory to leave the results of Eq. (34) in parametric form rather than combining them into a single expression. We begin the derivation by defining a new variable  $X$  by

$$X = \sum_{i=1}^3 R_i \rho_i, \quad (35)$$

and we may then rewrite Eq. (1) as  $(n^2 - 1)/(n^2 + 2) = X$ , which may be solved for  $n$  and for  $(n - 1)$ . The derivative required in Eq. (34) is evaluated by using  $dn/d\sigma = (dn/dX)(dX/d\sigma)$ , giving

$$dn/d\sigma = (3Y/2)[(1 - X)(1 - X)^{1/2}(2X + 1)^{1/2}]^{-1}, \quad (36)$$

in which

$$Y = \rho_1(dR_1/d\sigma) + \rho_2(dR_2/d\sigma) + \rho_3(dR_3/d\sigma). \quad (37)$$

Hence, we have

$$(n^G - 1) = \frac{3X}{(2X + 1)^{1/2}(1 - X)^{1/2} + (1 - X)} + \sigma \frac{3Y}{2} [(1 - X)(1 - X)^{1/2}(2X + 1)^{1/2}]^{-1}. \quad (38)$$

For the next step, the evaluation of  $dR_i/d\sigma$ , we rewrite

**Table IV. Comparison of Refractivity Formulas**

I. Pressure dependence				
Conditions: 6328 Å, 0% R.H., 15°C				
Refractivity × 10 <sup>6</sup>				Difference, Edlén vs general formula
<i>P</i> , mb	General formula	Simplified formula	Edlén	
250	68.202	68.202	68.201	-0.001
500	136.418	136.419	136.418	0.000
1000	272.900	272.900	272.900	0.000
1500	409.445	409.443	409.445	0.000

II. Temperature dependence				
Conditions: 6328 Å, 0% R.H., 1000 mb				
Refractivity × 10 <sup>6</sup>				Difference, Edlén vs general formula
<i>T</i> , °C	General formula	Simplified formula	Edlén	
-30	323.616	323.617	323.551	-0.065
-15	304.731	304.731	304.705	-0.026
15	272.899	272.900	272.900	+0.001
45	247.104	247.105	247.093	-0.011
60	235.957	235.957	235.932	-0.025

III. Humidity dependence				
Conditions: 6328 Å, 1000 mb, 15°C				
Refractivity × 10 <sup>6</sup>				Difference, Edlén vs general formula
R.H., %	General formula	Simplified formula	Edlén	
0	272.899	272.900	272.900	+0.001
50	272.534	272.535	272.542	+0.008
100	272.171	272.171	272.183	+0.012

Conditions: 6328 Å, 1000 mb, 45°C				
Refractivity × 10 <sup>6</sup>				Difference, Edlén vs general formula
R.H., %	General formula	Simplified formula	Edlén	
0	247.104	247.105	247.093	-0.011
50	245.262	245.261	245.077	-0.185
100	243.452	243.451	243.061	-0.391

the definition in Eq. (2) of  $R_i$  as

$$R_i = [(\rho_0)_i]^{-1} (r_i A_i / B_i), \quad (39)$$

in which

$$A_i = r_i - 2$$

$$B_i = r_i A_i - 3.$$

After some manipulation, it may be shown that

$$(dR_i/d\sigma) = 6(dr_i/d\sigma)[(\rho_0)_i R_i B_i - r_i]/(\rho_0)_i B_i^2 r_i. \quad (40)$$

Expressions for the quantities  $r_i$  ( $i = 1, 2, 3$ ) and  $\rho_i$ , and the conditions for which  $\rho_i$  are to be evaluated to give  $(\rho_0)_i$ , are given in Table III. The derivatives  $dr_i/d\sigma$  may be shown to be

$$\frac{dr_1}{d\sigma} \times 10^8 = 2\sigma \left[ \frac{2,405,640}{(130 - \sigma^2)} + \frac{15,994}{(38.9 - \sigma^2)} \right]$$

$$\frac{dr_2}{d\sigma} \times 10^8 = 2\sigma [2.6422 - 0.064760\sigma^2 + 0.012084\sigma^4] \quad (41)$$

$$\frac{dr_3}{d\sigma} \times 10^8 = 2\sigma \left[ 117.8 + \frac{2,406,030}{(130 - \sigma^2)} + \frac{15,997}{(38.9 - \sigma^2)} \right].$$

Using  $r_i$ ,  $dr_i/d\sigma$ , and  $(\rho_0)_i$ , the quantities  $R_i$  and  $dR_i/d\sigma$  may be found, and then  $X$  and  $Y$ . Substitution into Eq. (38) yields  $(n^\sigma - 1)$ .

A simplified formula for group refractive index may be found by substituting Eq. (29) into Eq. (34). The result is

$$(n^\sigma - 1) \times 10^8 = \left[ 2371.34 + 683,939.7 \frac{(130 + \sigma^2)}{(130 - \sigma^2)^2} + 4547.3 \frac{(38.9 + \sigma^2)}{(38.9 - \sigma^2)^2} \right] D_s + [6487.31 + 174.174\sigma^2 - 3.55750\sigma^4 + 0.61957\sigma^6] D_w, \quad (42)$$

in which  $D_s$  and  $D_w$  are given by Eqs. (30) and (31), respectively. A comparison of the group refractivities obtained from the full formula, from Eq. (42), and from Edlén's formula is given in Table V. No table showing pressure dependence is included because the formulas all agree to within  $0.2 \times 10^{-8}$ . It may be seen that the full formula and Edlén's agree slightly less well than in the case of phase refractive index, and in addition that there are deviations between the full formula and the simplified one at high temperatures and humidities, the difference being  $1.6 \times 10^{-8}$  at 1000 mb, 45°C, 100% R.H., and 3650 Å.

## V. Application to Optical Distance Measurement

At present, one of the main limitations to the accuracy of optical length measurements through the uncontrolled atmosphere is the uncertainty in the average refractive index over the optical path due to nonuniformity and turbulence of the atmosphere. Satisfactory results can be obtained over short distances by using meteorological measurements at one or more points along the path, but accuracies of  $1 \times 10^{-6}$  and better are difficult to obtain outdoors over distances greater than a few tens of meters.

It has been suggested<sup>16</sup> that simultaneous measurements of optical distance over the same path using two different wavelengths of light could be used to provide the required correction. Such measurements give the average dispersion over the path, from which the average refractive index can be calculated using a suitable dispersion formula. For path lengths of a few tens of meters, direct interferometry may be used as described by Erickson.<sup>2</sup> A simple example may be

**Table V. Comparison of Group Refractivity Formulas**

**I. Temperature dependence**

Conditions: 3658 Å, 0% R.H., 1000 mb

T, °C	Group refractivity × 10 <sup>6</sup>			Difference, Edlén vs general formula
	General formula	Simplified formula	Edlén	
-30	364.272	364.271	364.197	-0.075
-15	343.014	343.013	342.983	-0.031
15	307.183	307.182	307.183	0.000
45	278.147	278.147	278.133	-0.014
60	265.600	265.599	265.571	-0.029

**II. Humidity dependence**

Conditions: 3658 Å, 15°C, 1000 mb

R.H., %	Group refractivity × 10 <sup>6</sup>			Difference, Edlén vs general formula
	General formula	Simplified formula	Edlén	
0	307.183	307.182	307.183	0.000
100	306.593	306.589	306.582	-0.011

Conditions: 3658 Å, 45°C, 1000 mb

R.H., %	Group refractivity × 10 <sup>6</sup>			Difference, Edlén vs general formula
	General formula	Simplified formula	Edlén	
0	278.147	278.147	278.133	-0.014
100	275.206	275.190	274.756	-0.450

given to illustrate this method. Consider an automatic fringe-counting Michelson interferometer illuminated by 4546 Å radiation from an argon ion laser and by 6328 Å radiation from a helium-neon laser. If one of the mirrors is moved a distance  $\Delta L$ ,  $N_1$  fringes will be counted for wavelength  $\lambda_1$  and  $N_2$  for wavelength  $\lambda_2$ . The dispersion of air will cause the difference in the number of counts per count for  $\lambda_1$ ,  $(N_1 - N_2)/N_1$ , to depend on the average air density. It may be shown that

$$\left(\frac{N_1 - N_2}{N_1}\right)_{\text{air}} - \left(\frac{N_1 - N_2}{N_1}\right)_{\text{vacuum}} = \frac{\lambda_1}{\lambda_2} \left(1 - \frac{n_1}{n_2}\right), \quad (43)$$

where  $\lambda_1$  and  $\lambda_2$  are the wavelengths measured in vacuum. A measurement of the difference in the number of fringes for  $\lambda_1$  and  $\lambda_2$  per fringe of  $\lambda_1$  may thus be used to find the ratio  $n_1/n_2$  and hence the average air density. The accuracy of fringe-counting required to give  $(n_1 - 1)$  to one part in two hundred and eighty is  $1 \times 10^{-8}$ , or about 0.04 fringe/m. For path lengths of several kilometers, such as geodetic baselines, direct interferometry is impractical and modulated light tech-

niques are used instead. The application of the dual wavelength method to this type of measurement has also been described.<sup>3</sup>

Because a large dispersion is desirable for these techniques and the measurements are made outdoors, a dispersion formula valid over a wide range of wavelengths and conditions is required. It may be shown that the dispersion in group refractive index  $[n^g(\lambda_1) - n^g(\lambda_2)]$  given by Edlén's formula is 0.25% low compared to that given by the new formula for  $\lambda_1 = 3650$  Å and  $\lambda_2 = 6328$  Å at 1000 mb, 45°C, and 100% R.H. It should be noted that the dual wavelength methods require the use of only relative refractivity,  $[n(\lambda_1) - 1]/[n(\lambda_2) - 1]$ , and hence the errors due to the use of Edlén's formula will partially cancel, and the errors due to the assumption of the Lorentz field should largely cancel. In support of the latter argument, Erickson<sup>10</sup> has found experimentally that the relative refractivity of dry air varies by less than  $3 \times 10^{-6}$  for a change in pressure of 0.5 atm.

## VI. Summary

An analysis of the density and composition dependence of the refractive index of air based on the Lorenz-Lorentz equation has been carried out, and new formulas for both phase and group refractive index which are useful over a wide range of pressure, temperature, and composition have been derived. Simplified formulas are also presented. Although Edlén's recently suggested formula for phase refractive index is shown to be adequate for all reasonable pressures and for the range of temperatures and humidities normally encountered, the new formulas are significantly more accurate under conditions of high temperature and high humidity. New methods of optical length measurement through the uncontrolled atmosphere which require accurate refractivity formulas are briefly discussed.

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based on a wave-length of light from a krypton-86 lamp; but the bar is still a most valued measuring tool.

The meter bar and kilogram were brought to this country in 1890 to serve as the U.S. standards for length and mass. They were fabricated in France under the agreement, called the Treaty of the Meter, which tied together the measurement systems of twenty nations (now forty). President Harrison personally accepted the meter bar and kilogram for this country. In 1901, they were placed in the custody of the newly created National Bureau of Standards, and, in 1903, moved with NBS into its Connecticut Avenue site. So valuable and delicate are these two standards that, even during their long stay in the vault at Connecticut Avenue, they were taken out less than once a year,

usually to check the value of some lesser standards or to be checked themselves against the world standards kept in Paris. The kilogram standard has been back to Paris only twice and the meter bar four times during the past seventy-five years.

The new complex was dedicated on 15 November 1966, with Secretary of Commerce John T. Connor heading the list of dignitaries from government, science, and industry joining in the ceremonies. In conjunction with the dedication, Secretary Connor sponsored a two-day symposium on Technology and World Trade with some 500 participants from all over the world.

The National Bureau of Standards last year began distribu-

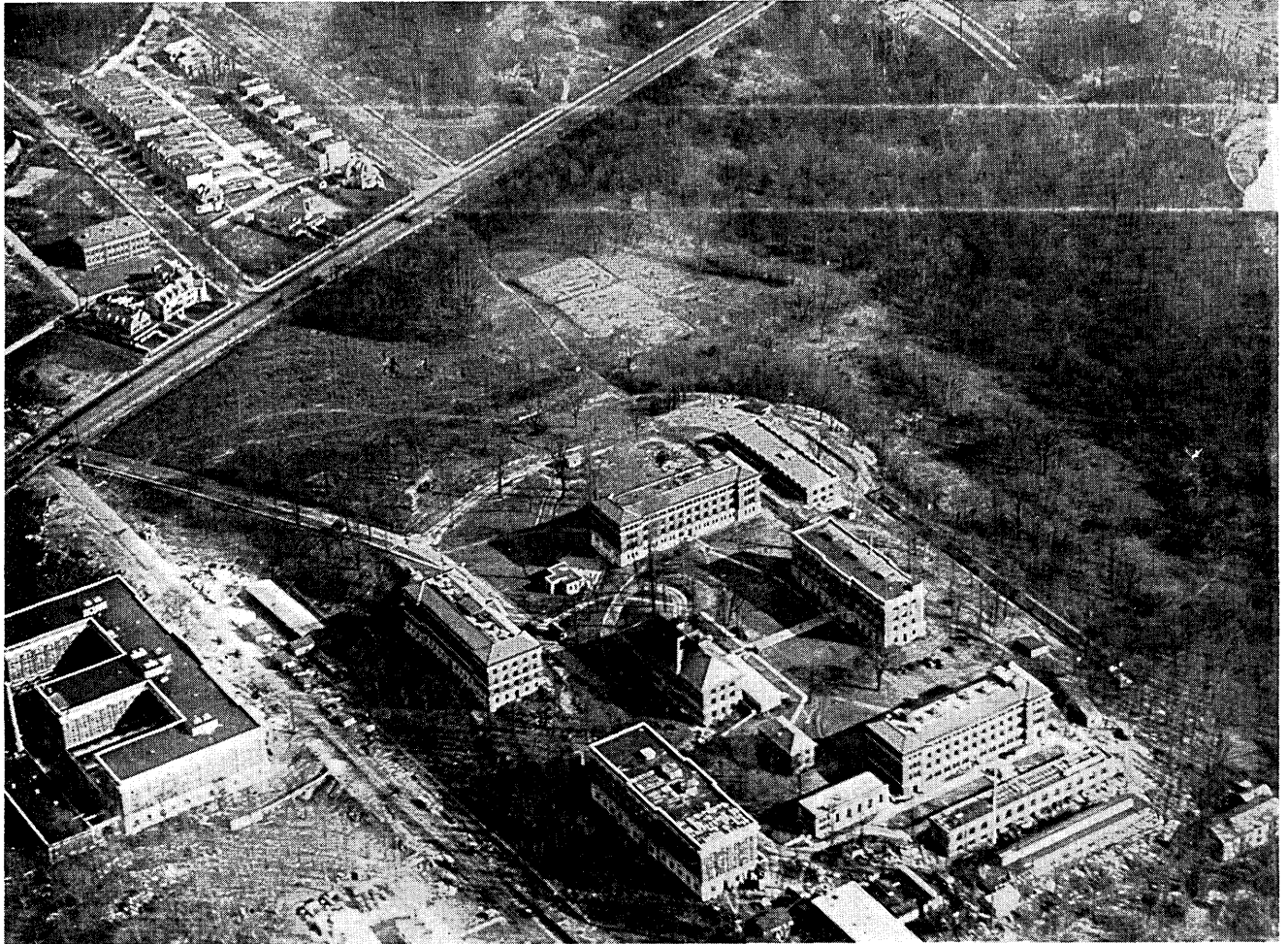


Fig. 1. Photograph of National Bureau of Standards (looking southeast), made by William F. Meggers in 1919 on Cramer Spectrum Process Plate, from a Curtis training plane at 305 m. *Note:* Industrial Laboratory in lower left corner (interior still unfinished) and a country store with gas station just above (at intersection of Connecticut Avenue and Van Ness Street). There are few automobiles on grounds or streets; and absolutely no car parking areas. The cultivated area just above center represents the victory gardens of patriotic workers during and following World War I. There is no Tilden Street west of Connecticut Avenue.