



## The Refractive Index of Air

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Table 17. Differences between thermodynamic scale and IPTS

$t_{\text{int}}^{\circ}\text{C}$	$t_{\text{th}} - t_{\text{int}}$ in $^{\circ}\text{C}$								unweighted mean
	gas thermometer						radiation		
	Ho (1901)	Da (1910)	Oi (1956)	Go (1960)	Ki (1964)	Mo (1962)	Heu (1964)	Ha (1965)	
1063	0.8	-0.3	0.7 <sub>1</sub>	1.5 <sub>4</sub>	1.20	1.4 <sub>8</sub>	1.4	0.7	0.9 <sub>4</sub>
960.8	1.0	-0.5	0.4 <sub>8</sub>			1.1 <sub>3</sub>	1.4	0.4	0.6 <sub>5</sub>
660						0.3 <sub>1</sub> **	0.3 <sub>3</sub>	0.1 <sub>5</sub> **	0.2 <sub>6</sub>

$t_{\text{th}}$  = thermodynamic temperature in  $^{\circ}\text{C}$ .

$t_{\text{int}}$  = temperature on the IPTS in  $^{\circ}\text{C}$ .

Ho = HOLBORN and DAY, [Ho 00], [Ho 01] and [He 51].

Da = DAY and SOSMAN, [Da 10], [He 51].

Oi = OISHI et al., [Oi 56].

Go = GORDOW et al., [Go 60].

Ki = KIRENKOW et al., [Ki 64].

Mo = MOSER et al., [Mo 62].

Heu = HEUSINKVELD, [He 64].

Ha = HALL, [Ha 65].

\*\* Graphical interpolation.

from gas thermometer and radiation measurements at 660°, 960.8° and 1063 °C. The estimated uncertainties in the values of the gold point and the silver point, as given by the investigators, are for the older gas thermometer measurements 0.8° (HOLBORN, DAY) and for the more recent one's 0.05° (OISHI), 0.1° (MOSER) and 0.2° (GORDOW, KIRENKOW). The estimated errors in the results of the radiation measurements are 0.4° (HEUSINKVELD) and 0.6° (HALL).

Considering the comparatively great discrepancies in the data of Tab. 17 in view of the small estimated errors, it is clear that undetected systematic errors must have affected some of the results, e.g. for the gas thermometer a possible error in the determination of the bulb temperature or in the mean linear expansion coefficient of the bulb material. It is difficult to assign weights to the different results.

The best that can be said for the time being is that the present value of the gold point, 1063 °C, needs a correction of 0.7 to 1.5 degree. More information on the magnitude of some systematic errors in gas thermometer and radiation measurements is needed to know the definite value of the gold point on the Thermodynamic Temperature Scale.

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\* This thesis can be obtained from the Library of the Physics Laboratory of the University.

## The Refractive Index of Air

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### Abstract

Present knowledge of the refractive index of air is reviewed. Regarding the absolute values there are as yet no definite indications that the standard adopted in 1953 on the basis of Barrell and Sears' measurements should be changed, but new experiments aiming at reducing the present uncertainty of about  $\pm 5 \times 10^{-8}$  would be desirable.

Several recent investigations have contributed important new information on the dispersion of air, which has made it possible to derive an improved dispersion formula for standard air,

$$(n - 1)_s \times 10^8 = 8342.13 + 2406030 (130 - \sigma)^{-1} + 15997 (38.9 - \sigma)^{-1},$$

where  $\sigma$  is the vacuum wave-number in  $\mu\text{m}^{-1}$ . The deviations

from the 1953 formula are small and practically negligible in most spectroscopic work.

An equation for the dependence of refractivity on temperature and pressure based on theoretical considerations has been derived. For the range of atmospheric conditions normally found in a laboratory the equation can be approximated by the formula

$$(n-1)_{tp} = (n-1)_s \times 0.00138823 p / (1 + 0.003671 t),$$

with  $p$  in torr,  $t$  in °C, and  $(n-1)_s$  given by the dispersion formula for standard air.

The effect of carbon dioxide and water vapour is discussed. From Erickson's dispersion data for water vapour, combined with Barrell and Sears' absolute measurements, one obtains the equation  $n_{tp} - n_s = -f (5.722 - 0.0457 \sigma^2) \times 10^{-8}$  for the difference in refractive index of moist air, containing  $f$  torr of water vapour, and dry air at equal temperature and total pressure. The equation is valid for visible radiations and normal atmospheric conditions.

### Introduction

The refractive index of air affects the wavelengths of electromagnetic radiations through the relation  $n\lambda_{\text{air}} = \lambda_{\text{vac}}$ , and a knowledge of  $n$  is therefore always required when measurements involving light wavelengths are made in air. In spectroscopy this was a point of fundamental importance when the primary standard of wavelengths was defined in "standard air", that is, dry air at 760 torr and 15 °C. In fact, this definition of standard air appears to have originated in connection with the creation of the primary standard of wavelengths some 60 years ago when 15 °C was considered an average laboratory temperature. In the present situation, with the primary standard defined in the vacuum, the refractive index of air plays a less fundamental role but remains indispensable as long as most spectroscopic measurements are being made in air.

The formula for the refractivity of standard air that has been accepted as standard for some time was derived in 1951 (EDLÉN 1953). In the meantime there have been published investigations by RANK et al. (1958), SVENSSON (1960), PECK et al. (1962) and ERICKSON (1961), which have provided new information on the dispersion of air, and by ERICKSON (1961) on the dispersion of water vapour. It has appeared timely, therefore, to review the present situation concerning the refractive index of air. The following discussion will include the absolute refractivity, the dispersion formula, the dependence on temperature and pressure, and the effect of variable contents of carbon dioxide and water vapour. The dependence of the refractive index on atmospheric conditions would be important especially in connection with optical length measurements over long distances in the open air that are now being contemplated by use of laser techniques.

#### The absolute refractivity of standard air

##### *Experimental data and the adopted value*

At the time when the 1953 dispersion formula was derived the most recent and apparently most accurate absolute determinations of the refractivity of air were those by PÉRARD (1934) at BIPM, KÖSTERS and LAMPE (1934) at PTR, and BARRELL and SEARS (1939) at NPL. The results of PÉRARD confirmed those of BARRELL and SEARS within the statistical errors, while KÖSTERS and LAMPE's values were higher by an amount that seemed to exceed the error limits for the other two measurements as estimated from the

detailed reports on the experiments. The details of KÖSTERS and LAMPE's work have never been published, and their brief report does not even give an error estimate. These circumstances induced me to choose BARRELL and SEARS' data, which showed a higher consistency than those of PÉRARD, as the absolute basis for the 1953 dispersion formula. The subsequent adoption of this formula by the Joint Commission for Spectroscopy, the Advisory Committee for the Definition of the Metre, and the Commission 14 of the International Astronomical Union has given a sort of codification to this choice of absolute refractivity.

No satisfactory explanation has yet been obtained for the discrepancy between the PTR results and those of BIPM and NPL. The earlier discussion of this question (EDLÉN, 1953) included some information received from Dr. ENGELHARD regarding the probable experimental circumstances of the PTR measurements. In the meantime the complete records of the experiments have been found. According to these records, as we are now informed by Dr. ENGELHARD (private letter, November, 1965), KÖSTERS and LAMPE had not been using "synthetic" air but natural air deprived of CO<sub>2</sub> and H<sub>2</sub>O by means of KOH, CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>. The contamination by oil vapours, which was considered a likely possibility in the PTR experiment, would presumably have affected both the air-filled and the evacuated path so that the effect would tend to become compensated. On the other hand, the discovery by SVENSSON (1960) that silica gel has a tendency to reduce the relative nitrogen content has disclosed a possible cause for the values of BARRELL and SEARS to be low since they used silica gel as drying agent. However, this argument does not apply to PÉRARD's results which are equally low. Thus, the evidence is inconclusive, and the question whether the low or the high values are the more correct remains undecided.

More recently, KORONKEVICH (1956) has published a formula based on absolute measurements in the visible and lying about  $7 \times 10^{-8}$  higher than the 1953 formula. It is difficult to judge whether the difference is significant in comparison with experimental errors. PECK and collaborators have made absolute determinations in connection with their dispersion measurements in the infrared (see next section). In their first publication (SCHLUETER and PECK 1958) the result is higher than the 1953 formula by  $4.4 \times 10^{-8}$ , while in the final publication (PECK and KHANNA 1962) it is lower than the formula by  $5.2 \times 10^{-8}$ . The authors consider the differences to lie within their experimental errors.

It is of interest to mention, also, the refractivity determinations made at the BIPM in the course of interferometric measurements of mechanical length standards as described by TERRIEN (1965). Each length measurement with the BIPM comparator involves a simultaneous determination of the refractivity of the air in the comparator enclosure at the actual temperature, pressure and composition. In the example given by TERRIEN, the refractivity at 6058 Å was found to be  $22 \times 10^{-8}$  larger than the value calculated by adjusting the 1953 formula to the measured temperature, pressure and humidity. Quoting TERRIEN we note that "this difference is the largest observed; it may happen to be much smaller, almost zero, but the measured value has always been larger than the

calculated value. This difference may be attributed chiefly to contamination of the air, and partly to error in EDLÉN's formula (or also, of course, to unsuspected errors in the measurements reported here). The air came from a clean but sparingly ventilated room, and was enclosed for more than one day in a heavily lagged 20 m<sup>3</sup> airtight tank containing an elaborate mechanical comparator". The errors in the measurements of pressure and humidity and their possible contribution to the reported differences have not been discussed in the paper. If we can neglect these errors we would expect to find high values in these measurements, since the most likely changes in the composition of the air (replacement of O<sub>2</sub> by CO<sub>2</sub>, and contamination with oil and varnish vapours) would all increase the refractivity as compared to standard air. The wide range of the differences, from almost zero to about  $20 \times 10^{-8}$ , is somewhat surprising, but may be considered as showing how variable the composition can be. It appears, therefore, that these experiments give little information regarding a possible error in the 1953 formula, but they do emphasize the necessity of eliminating air refractivity in interference length measurements by determining  $n$  of the actual air *in situ*.

#### *Implications of an error in the adopted refractivity of standard air*

Although it cannot be concluded with certainty from the above discussion whether the adopted refractivity should be raised or lowered, the indications are perhaps somewhat in favour of raising it. The figure  $\pm 5 \times 10^{-8}$  mentioned by TERRIEN (1965) as an estimate of the uncertainty in the absolute refractive index appears reasonable. Since the relative values of  $(n - 1)$  for different wavelengths are known with a much higher accuracy (see next section) a possible correction to the absolute values would take the form of multiplying  $(n - 1)$  by a constant factor. As far as spectroscopy is concerned it would then be most convenient to include this correction in the density factor by redefining, for example, the temperature of standard air. There is nothing fundamental about the present value of 15 °C, and it would certainly be easier to change this figure than to revise existing tabulations of air wavelengths and conversion tables.

In interference metrology, as was shown by TERRIEN, the difficulties of measuring in air a material length standard in terms of vacuum wavelengths depend more on the uncertainty about the state of the actual air than on the error in the adopted refractivity of standard air. The rational solution has been found in combining the length measurement with a simultaneous refractivity determination of the ambient air, which eliminates the need of knowing the refractivity of standard air.

The refractive index of standard air was involved in the procedure used by the Advisory Committee in redefining the metre in 1957. Thus, the wavenumber of the krypton line that was to define the new metre was derived by interferometric comparison with the vacuum wavelength of the red cadmium line, the latter having been obtained from its value as defined in standard air, 6438.4696 Å, by using the refractive index given by the 1953 formula. By choosing this procedure, rather than a direct evaluation of the

prototype metre in vacuum wavelengths of the krypton line, the long accepted scale of light wavelengths was to be conserved to the highest possible accuracy at the same time as the less precisely defined scale based on the metre bar would be conserved within its wider error limits. The old metre has later been evaluated by HART and BAIRD (1961) by measuring directly in terms of the krypton wavelength four different length standards with known relation to the prototype metre. The result indicated that "the metre, according to the new definition, is shorter than the metre as formerly defined by  $0.2 \mu\text{m}$  to within  $\pm 0.2 \mu\text{m}$ ". This would imply that the wavenumber of the krypton line,  $1650763.73 \text{ m}^{-1}$ , accepted as the new definition of the metre, was too small by  $(0.35 \pm 0.35) \text{ m}^{-1}$ , or its wavelength too large by  $(0.0013 \pm 0.0013) \text{ \AA}$ . Consequently, as the error in the intercomparison of the krypton and the cadmium wavelengths may be supposed to have been considerably smaller, the adopted vacuum wavelength of the red cadmium line was too large by  $(0.0014 \pm 0.0014) \text{ \AA}$ . If this difference should be ascribed to an error in the adopted refractive index, the latter should have been too large by  $(20 \pm 20) \times 10^{-8}$ . The amount is several times the estimated error limits ( $\pm 5 \times 10^{-8}$ ) and the sign is opposite to what some other indications suggest. This seems to prove that the particular choice of refractive index has no significant part in a possible difference between the old and the new metre. Such a difference, if it exists, must derive essentially from the accepted relation between the standard-air value of the cadmium wavelength and the prototype metre.

While it appears from this discussion that the present uncertainty in the absolute values of the refractive index of air would have no serious consequences either in spectroscopic work or in laboratory metrology, it is possible that need of more precise values may arise in connection with recent efforts to apply optical methods to geodetic length measurements (ERICKSON, 1962; BENDER and OWENS, 1965). This gives a motivation for renewed attempts to determine the absolute refractive index with a precision corresponding to present experimental techniques and present experience of the various sources of error, especially those connected with the composition of the air.

#### **The dispersion formula for standard air**

The refractivity,  $n - 1$ , for a gas can be expressed to a high degree of approximation as the product of a dispersion factor, depending on  $\lambda$  only, and a density factor which is independent of  $\lambda$ . This was demonstrated by BARRELL and SEARS' (1939) measurements and was proved more accurately by SVENSSON (1960) as regards the invariance of the dispersion with temperature and by ERICKSON (1961) as regards pressure. Consequently, the dispersion factor can be determined by relative measurements without accurate knowledge of temperature and pressure. Also, because of the comparatively close similarity of the  $\lambda$ -dependence for various gases, the dispersion factor is less sensitive than the absolute refractivity to deviations from the correct composition of the gas sample. As a result, the dispersion of air can be determined with a much higher accuracy than its absolute refractivity.

*New observations on the dispersion of air*

The 1953 dispersion formula had been obtained by adjusting the relative measurements of KOCH (1912) and TRAUB (1920), covering the ultraviolet spectrum, to the absolute values given by BARRELL and SEARS (1939) for the visible region. It was estimated from the scatter of the points that the derived formula should be accurate as regards relative values of  $n$  to about  $\pm 1 \times 10^{-8}$  over the whole region of interest, that is, from about 2000 Å up to as long wavelengths as can be observed with infrared detectors. As the measurements on which the formula was based were limited to the region from 1854 to 6440 Å, the infrared part of the curve was an extrapolation. A check on this extrapolation, as well as on the old data for the ultraviolet, was clearly desirable.

In the meantime there have been published four different investigations which together have provided improved information on the dispersion of air over the range from 2300 Å to 20000 Å. These new data, which we shall discuss presently, have confirmed the 1953

Table 1. *Recent investigations of the dispersion of air*

Nr.	Author	Interferometer	Length of light path	Wavelength range	Number of lines
1	RANK et al. (1958)	MICHELSON	2 × 1 m	3651 — 15299 Å	8
2	PECK et al. (1962)	MICHELSON	2 × 0.24 m	5462 — 20586 Å	13
3	SVENSSON (1960)	JAMIN	1 × 1 m	2302 — 6909 Å	26
4	ERICKSON (1961)	MICHELSON	2 × 14 m	3889 — 6440 Å	10

formula practically within the error limits originally estimated, and, at the same time, have made it possible to draw the dispersion curve with considerably narrower error limits.

The investigations referred to are briefly characterized in Tab. 1. The instruments used in the experiments numbered 1, 2 and 4 can be described as modified Michelson interferometers with corner reflectors, in nr. 1 and 4 with the two light beams folded into a nearly parallel position. The length of the light path gives an indication of the potential accuracy, but the disadvantage of the short path used by PECK et al. was somewhat compensated by their fringe interpolator which permitted reading the fractional part of fringes to a high accuracy. In nr. 1, 3 and 4 the observations were made photographically except for the measurement at 15299 Å by RANK et al. In this case, as well as in all the observations by PECK et al., photoconductive cells or photomultipliers were used as detectors. The air was dried by freezing in nr. 2 and by using P<sub>2</sub>O<sub>5</sub> in nr. 3. ERICKSON made a special investigation of the composition of his air sample and corrected his data for the slight deviations from that of standard air. RANK et al. only state that they used dry, CO<sub>2</sub>-free air. The effect on the dispersion curve of the removal of the normal CO<sub>2</sub> content is negligible within their error limits. There is no apparent reason for suspecting that the results of anyone of the four investigations should have been affected by errors in the composition of the air to an extent that would be significant in comparison with their respective experimental errors.

As a first step in utilizing the new data to improve the dispersion formula they have to be normalized. In view of the high consistency of ERICKSON's results,

indicating an order of magnitude higher accuracy than can be claimed for any of the other measurements, we take ERICKSON's data to define the dispersion curve through the visible range. Since the slope of this curve shows a distinct deviation from that of the 1953 dispersion formula, we shall first adjust ERICKSON's values to a suitable absolute level, and then normalize all the other data to this new curve rather than to the 1953 formula. As regards the choice of the crossing point of the old and the new curve there may be arguments for conserving the refractivity value at the former primary standard,  $\lambda$  6440, or at the present one,  $\lambda$  6058. We have chosen the latter point, thereby introducing a change in the refractivity at 6440 Å of about  $+ 0.1 \times 10^{-8}$  which is quite immaterial. By this procedure we obtain the experimental data collected in Tab. 2. The first column gives the wavelength at which the refractivity was measured, the second column gives the corresponding value of  $(n - 1)$  according to the 1953 formula, and then follow the differences (in  $10^{-8}$ ) between the normalized observed

values of the four new investigations\* and the 1953 value. In the last column we give the corrections to the 1953 values as implied by a formula derived on the basis of the new observations. The change in slope in the visible range and the choice of crossing point cause an average lowering of  $(n - 1)$  for visible radiations by about  $0.4 \times 10^{-8}$ . This means a corresponding departure from the absolute level as defined by BARRELL and SEARS' data, but the shift is negligible in comparison with the estimated error limits ( $\pm 5 \times 10^{-8}$ ) of the absolute values. In fact, the use of an alternative density factor in the evaluation of BARRELL and SEARS' observations (see next section) would lower their values by  $0.9 \times 10^{-8}$ .

Most of the new data have been plotted in Fig. 1, where TRAUB's values are also included as still being the only ones available below 2300 Å. Since ERICKSON's data are so much superior we have not plotted those of BARRELL and SEARS or of RANK et al. in the visible region. The latter are the more consistent of the two, and both sets are in accord with ERICKSON's curve within their experimental uncertainty. It is interesting to note, also, that the trend exhibited by the differences between observed and calculated fringe numbers in the BIPM measurements (TERRIEN, 1965) agrees with the slope of the new dispersion curve. The scatter of the points taken from SVENSSON's work, though large in comparison with the other new measurements, is much smaller than in KOCH's data (cf. SVENSSON, 1960, Fig. 4), which, therefore, have been replaced by SVENSSON's values.

\* The figures given in Tab. 2 and plotted in Fig. 1 were obtained in the following way. The value at 15299 Å of RANK et al. (1958, Tab. 1) was increased by the factor 27789.9/27785.6 = 1.000155, and all the other values of the same authors (1958, Tab. 2) were multiplied by 1.000150. The values given by PECK and KHANNA (1962, Tab. 1) were reduced by  $0.19 \times 10^{-8}$  and the result rounded off to one decimal. SVENSSON's values (1960, Tab. 6) were reduced by  $0.3 \times 10^{-8}$ . ERICKSON's values (1961, Tab. 10) were made to coincide at 6058 Å with the 1953 formula by multiplying with 0.9999930, the correction ranging from  $- 0.193 \times 10^{-8}$  at 6440 Å to  $- 0.198 \times 10^{-8}$  at 3889 Å, and rounded off to two decimals. TRAUB's values were taken from EDLÉN (1953) and multiplied by 1.000162.

Table 2. Normalized data from recent dispersion measurements

$\lambda_{\text{vac.}}$	1953 formula ( $n - 1$ ) $\times 10^8$	RANK et al. — 1953	PECK et al. — 1953	SVENSSON — 1953	ERICKSON — 1953	1965 — 1953
20586.91	27296.22		(- 0.1)			+ 1.2
16945.21	27313.55		+ 0.4			+ 1.1
15299.77	27325.8	+ 0.3				+ 1.1
15293.54	27325.80		+ 0.4			+ 1.1
14756.50	27330.70		+ 0.1			+ 1.1
13722.33	27341.84		+ 0.4			+ 1.0
13507.88	27344.48		+ 0.7			+ 1.0
11290.50	27381.21		- 0.1			+ 0.9
10142.57	27410.45		+ 0.3			+ 0.8
9125.47	27446.25		+ 0.3			+ 0.7
7247.16	27557.20		- 0.1			+ 0.3
7034.35	27575.79		(+ 1.1)			+ 0.3
6909.66	27587.5			- 1.1		+ 0.3
6718.29	27606.8			- 0.4		+ 0.2
6440.25	27638.07				+ 0.12	+ 0.1
6236.10	27663.8			+ 1.0		+ 0.1
6125.19	27678.9			- 1.1		0.0
6074.39	27686.1			+ 1.1		0.0
5792.26	27729.8	0.0				- 0.1
5771.20	27733.3	- 0.3				- 0.1
5677.47	27749.5			+ 0.2		- 0.1
5462.27	27790.07	- 0.3	- 0.2		- 0.19	- 0.2
5017.07	27891.90				- 0.37	- 0.4
4961.52	27906.7			- 1.7		- 0.4
4923.30	27917.12				- 0.42	- 0.4
4917.45	27918.8			- 0.1		- 0.4
4714.46	27979.11				- 0.50	- 0.5
4679.46	27990.36				- 0.52	- 0.5
4472.73	28062.66				- 0.58	- 0.6
4359.56	28106.95	- 0.4			- 0.66	- 0.7
4109.33	28219.2			- 0.8		- 0.8
4078.98	28234.3	- 0.7				- 0.8
4047.71	28250.34	- 0.8			- 0.81	- 0.8
3985.09	28283.6			- 0.8		- 0.8
3889.75	28337.62				- 0.83	- 0.8
3802.73	28390.8			- 0.3		- 0.8
3655.87	28490.3	- 0.7				- 0.8
3651.19	28493.7	- 0.8				- 0.8
3562.24	28560.9			- 1.4		- 0.8
3544.43	28575.0			- 0.6		- 0.8
3391.68	28706.7			- 0.8		- 0.7
2926.30	29264.5			- 0.2		- 0.2
2894.47	29314.6			- 0.2		- 0.1
2857.79	29374.7			+ 0.1		0.0
2760.59	29548.3			+ 0.4		+ 0.2
2753.60	29561.6			+ 0.5		+ 0.2
2675.75	29719.1			+ 0.7		+ 0.4
2577.11	29944.7			+ 0.8		+ 0.7
2464.82	30245.0			+ 0.7		+ 1.1
2447.65	30295.7			+ 1.6		+ 1.1
2379.11	30513.1			+ 1.3		+ 1.3
2346.17	30626.8			+ 1.5		+ 1.3
2302.89	30786.8			+ 0.8		+ 1.4

It is clear from Fig. 1 that the new dispersion measurements can be consistently combined to define a dispersion curve with significantly greater precision than in the case of the 1953 formula. It will be shown below how to represent this curve by a revised formula of the same type.

#### The derivation of a revised dispersion formula

The 1953 dispersion formula was expressed in the so-called Sellmeier form,  $(n - 1) = \sum_i A_i (\sigma_i^2 - \sigma^2)^{-1}$ , with three terms, one of which was reduced to a constant by neglecting  $\sigma^2$  in comparison with  $\sigma_i^2$ . The

$\sigma_i$ 's are the wave-numbers of certain resonance frequencies and  $\sigma$  is the running wave-number. In view of the much narrower tolerances of the new experimental data it was considered advisable first to try a complete 3-term formula, containing the six adjustable parameters  $A_1, A_2, A_3, \sigma_1, \sigma_2, \sigma_3$ , numbered in order of decreasing  $\sigma_i$ . The formula was fitted to the experimental data by adopting various combinations of fixed values for the  $\sigma_i$ 's, and determining for each such combination the coefficients  $A_i$  that made the formula pass through three judiciously chosen points. It was soon found that the value for  $\sigma_1$  is very flexible, but when changing  $\sigma_1$  one must change both  $\sigma_2$  and  $\sigma_3$  in the same direction as  $\sigma_1$ . It was also found that  $\sigma_3$  could be varied only within rather narrow limits, and that the short-wave part of the curve improved with increasing value of  $\sigma_3$ . Thus the formula improved as the value of  $\sigma_1$  increased, and the best result was

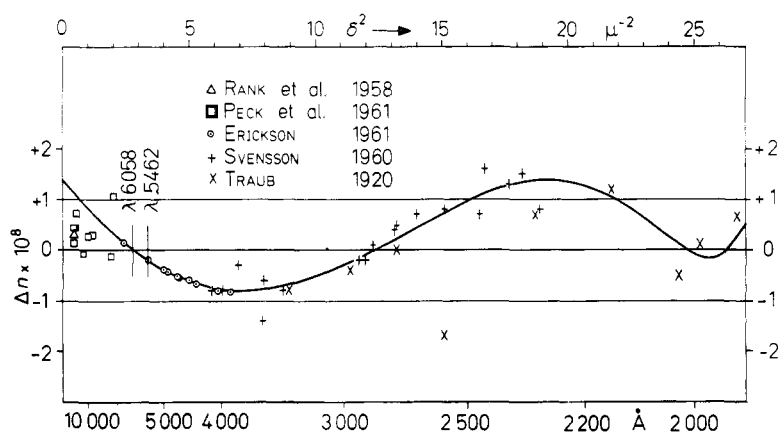


Fig. 1. Experimental basis for the dispersion formula for standard air. The zero line represents the 1953 formula

again obtained when  $A_1(\sigma_1^2 - \sigma^2)^{-1}$  was replaced by a constant. The finally accepted formula,

$$(n - 1)_s \times 10^8 = 8342.13 + 2406030 (130 - \sigma^2)^{-1} + 15997 (38.9 - \sigma^2)^{-1}, \quad (1)$$

where  $\sigma$  is the vacuum wave-number in reciprocal micrometres ( $\mu\text{m}^{-1}$ ), is shown in Fig. 1 to represent the observations from 2000 Å through the visible region in a very satisfactory way. The extremely small scatter of Erickson's points, the deviations being everywhere less than  $0.05 \times 10^{-8}$ , is a proof of the remarkable accuracy of his measurements. Even with a reasonable allowance for systematic errors due to the composition of his air sample, it would not be possible to change the extrapolated course of the curve through the infrared by much more than  $0.1 \times 10^{-8}$ . The infrared experimental values are seen to fall below the formula by an average of about  $0.7 \times 10^{-8}$ . This difference is well covered by the error limits ( $\pm 1.1 \times 10^{-8}$ ) given by RANK et al. for their value at 15299 Å. Regarding the values of PECK and KHANNA it should be noted that a deviation of  $0.7 \times 10^{-8}$  corresponds in their experiment to about 0.002 of a fringe. This would not seem so definitely outside a possible systematic error in their comparison of fringe numbers with the reference line at 5462 Å that one would have to assume a real inconsistency with ERICKSON's curve. Nevertheless, a further check on the infrared part of the curve would be of interest.

Some comments on the physical background of the derived formula may be instructive. First it should be remembered that the refractivity of air depends not on discrete absorption frequencies as assumed in the Sellmeier formula but on broad regions of continuous absorption. The last term in formula (1), with  $\sigma_3^2 = 38.9 \mu\text{m}^{-2}$  ( $\lambda_3 = 1603 \text{ Å}$ ), thus represents the effect of the dissociation continuum of  $\text{O}_2$ , which extends over some 400 Å with a maximum around 1450 Å. The second term, with  $\sigma_2^2 = 130$  ( $\lambda_2 = 877 \text{ Å}$ ), and the constant term together have to account for the large absorption continua of  $\text{N}_2$  and  $\text{O}_2$  which start around 1000 Å and extend to the X-ray region with a flat maximum somewhere around 500 Å. This helps to understand what physical meaning can be attached to the resonance frequencies in the Sellmeier equation and explains the flexibility of these frequencies. It should be noted, also, that the equation neglects the damping, which becomes of increasing importance as a resonance region is approached, and which may, in the region of 2000 Å and below, have a significant effect on that part of the refractivity which derives from the  $\text{O}_2$  dissociation continuum.

#### Comparison of the 1965 and the 1953 formulae

The new dispersion formula (1), which may be referred to as the 1965 formula, deviates from the 1953 formula by at most  $1.4 \times 10^{-8}$ , as is shown by the curve in Fig. 1, and a small change in absolute level would reduce the maximum deviation to  $\pm 1.1 \times 10^{-8}$ . This is as close a confirmation as could have been hoped

for. The deviations are about two orders of magnitude smaller than those of the previously used Meggers and Peters formula, and they are for most practical purposes immaterial. In order to judge the spectroscopic implications we show in Tab. 3 the quantities  $\Delta\lambda = \lambda\Delta n$  and  $\Delta\sigma = -\sigma\Delta n$  which give the changes in  $\lambda$  and  $\sigma$  corresponding to the deviations  $\Delta n = n(1965) - n(1953)$ . We find that  $|\Delta\lambda|$  does not exceed 0.00003 Å for wavelengths below 7700 Å, and  $|\Delta\sigma|$  does not exceed 0.0002  $\text{cm}^{-1}$  for wavelengths above 2600 Å. These amounts are hardly significant for measurements made in air. The primary standard now being defined in the vacuum, the most exacting wavelength intercomparisons are anyhow being made with evacuated interferometers. Consequently, a replacement of the 1953 formula as standard in spectroscopic work appears not to be an urgent necessity\*. In any case, one would like to be more certain of the course of the curve at the extreme ends of the spectral region, especially at the short-wave end, before taking the step of adopting a new formula.

In most applications of a dispersion formula an accuracy around  $10^{-8}$  in  $n$  is quite sufficient. For the visible and infrared regions formula (1) can easily be approximated to this accuracy by more convenient

\* Note that the  $\Delta\sigma$ 's in Tab. 3 do nowhere exceed 0.6 of the last decimal place of the NBS table of Wavenumbers (COLEMAN et al. 1960).

Table 3  
The corrections  $\Delta\lambda = \lambda\Delta n$  and  $\Delta\sigma = -\sigma\Delta n$ , corresponding to  
 $\Delta n = n(1965) - n(1953)$

$\sigma$ ( $\mu\text{m}^{-1}$ )	$\Delta\sigma \times 10^4$ ( $\text{cm}^{-1}$ )	$\lambda$ ( $\mu\text{m}$ )	$\Delta\lambda \times 10^6$ ( $\text{\AA}$ )
0		1.04	
0.39	0	0.98	+ 8
1.36	-1	0.93	+ 7
1.86	0	0.87	+ 6
2.29	+1	0.82	+ 5
3.23	+2	0.77	+ 4
3.44	+1	0.72	+ 3
3.60	0	0.68	+ 2
3.73	-1	0.63	+ 1
3.84	-2	0.58	0
3.97	-3	0.53	-1
4.07	-4	0.47	-2
4.22	-5	0.341	-3
4.59	-6	0.312	-2
4.69	-5	0.292	-1
4.76	-4	0.277	0
4.82	-3	0.263	+ 1
4.88	-2	0.249	+ 2
4.94	-1	0.217	+ 3
5.01	0	0.210	+ 2
5.11	+1	0.204	+ 1
5.15	0	0.193	0

Table 4. Approximations to formula (1)

Formula	Range	Max. error
$0.0472300(173.3 - \sigma^2)^{-1}$	4050 - 7050 $\text{\AA}$	$1.2 \times 10^{-8}$
$0.0480877(176.4 - \sigma^2)^{-1}$	$\lambda > 5800 \text{\AA}$	$0.7 \times 10^{-8}$
$(27260.6 + 155.7 \sigma^2) \times 10^{-8}$	$\lambda > 7050 \text{\AA}$	$0.8 \times 10^{-8}$
$(27261.1 + 154.3 \sigma^2) \times 10^{-8}$	$\lambda > 10000 \text{\AA}$	$0.2 \times 10^{-8}$

expressions, some examples of which are shown in Tab. 4. The constants  $\sigma^2$  in the one-term Sellmeier formulae correspond to wavelengths from 760 to 753  $\text{\AA}$ .

#### Refractivity as a function of temperature and pressure

The dependence of the refractive index of air on temperature and pressure was thoroughly discussed by BARRELL and SEARS (1939). They measured the refractivity for 8 wavelengths at 5 different temperatures from 12 °C to 30 °C, and for each temperature at 8 different pressures from 100 to 800 torr. From the 320 values thus obtained they derived an equation for the refractivity as a function of  $t$ ,  $p$  and  $\lambda$ . More recently, MASUI (1957) and SCHLUETER and PECK (1958) have proposed different expressions for the temperature and pressure dependence, based directly on the Lorenz-

Lorentz equation and the density equation for air. As there is, apparently, some uncertainty about this question, a review of the situation may be useful.

According to the Lorenz-Lorentz equation the function  $(n^2 - 1)/(n^2 + 2)$ , which for a gas can be approximated to  $(n - 1)[1 - (n - 1)/6] 2/3$ , is proportional to the density  $d$ . Writing the equation of state  $pV/RT = 1 - \varepsilon_t p$  we find  $d$  depending on  $t$  and  $p$  as  $p(1 + \varepsilon_t p)/(1 + \alpha t)$  with  $\alpha = 1/273.15$ . Consequently, we can write

$$(n - 1)_{tp} = K_\lambda D_{tp}, \quad (2)$$

where the dispersion factor  $K_\lambda$  is independent of  $t$  and  $p$ , and

$$D_{tp} = p(1 + \varepsilon_t p)/(1 + \alpha t) \left(1 - \frac{n-1}{6}\right). \quad (3)$$

$K_\lambda$  is here defined in accordance with BARRELL and SEARS. If  $p$  is measured in torr, as we shall assume in what follows, then  $K_\lambda$  represents the asymptotic value for low pressures of the refractivity *per torr*, at  $t = 0$  °C.  $D_{tp}$  shall be referred to as the density factor. Writing

$$D_{tp} = p(1 + \beta_t p)/(1 + \alpha t) \quad (4)$$

we have with sufficient approximation

$$\beta_t = \varepsilon_t + (n - 1)/6p, \quad (5)$$

and by introducing  $(n - 1) \approx K_\lambda p(1 - \alpha t)$ ,

$$\beta_t = \varepsilon_t + K_\lambda(1 - \alpha t)/6. \quad (6)$$

From the values of  $pV/RT$  for dry air tabulated by HILSENATH et al. (1955) we find that  $\varepsilon_t$  can be represented by the linear equation

$$\varepsilon_t = (0.750 - 0.0130_4 t) \times 10^{-6} \quad (7)$$

over the range 5 °C to 30 °C with an error less than  $10^{-8}$ . Thus we can write

$$\left. \begin{aligned} \beta_t &= a - bt, \\ a &= 0.750 \times 10^{-6} + K_\lambda/6, \\ b &= 0.0130 \times 10^{-6} + \alpha K_\lambda/6. \end{aligned} \right\} \quad (8)$$

For  $K_\lambda$  we take  $(n - 1)$  for standard air divided by  $760/(1 + 15\alpha)$ . The slight  $\lambda$ -dependence of  $a$  and  $b$  introduced by  $(n - 1)$  is found to be negligible for all purposes. By adopting suitable mean values of  $a$  and  $b$  as valid for all  $\lambda$  we get, finally,

$$\beta_t = (0.817 - 0.0133 t) \times 10^{-6}, \quad (9)$$

and

$$D_{tp} = p[1 + p(0.817 - 0.0133 t) \times 10^{-6}] / (1 + 0.0036610 t). \quad (10)$$

The expression (9) for  $\beta_t$  depends on the validity of the Lorenz-Lorentz relation and on the equation of state for dry air implied by (7)\*. The value of  $\varepsilon_t$  given by (7) agrees well with the value,  $\varepsilon_t = (0.751 - 0.0115 t) \times 10^{-6}$ , derived by BARRELL and SEARS from compressibility measurements of air by HOLBORN and SCHULTZE. However, instead of accepting this value of  $\varepsilon_t$  to obtain  $\beta_t$ , they adopted a value which they derived from their refractivity measurements, namely  $\beta_t = (1.049 - 0.0157 t) \times 10^{-6}$ , corresponding to  $\varepsilon_t = (0.985 - 0.0155 t) \times 10^{-6}$ . This is clearly outside the possible errors of (7), which means that one would have to accept a corresponding deviation from the Lorenz-Lorentz relation. As it seemed of interest

\* For the  $\text{CO}_2$ -free air used by BARRELL and SEARS the equation would not be noticeably different.



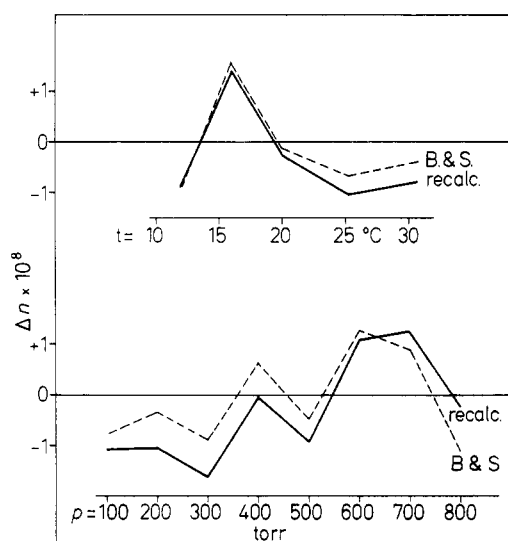


Fig. 2. Comparison of residuals ( $n_{\text{obs.}} - n_{\text{calc.}}$ ) in Barrell and Sears' refractivity data when adjusted with alternative density factors

to find out whether such a deviation is an unavoidable consequence of BARRELL and SEARS' measurements, we have reanalyzed the observational data given in their Tab. 8. First, the dispersion factor  $K_\lambda$  was determined from the forty observations for each wavelength by means of the equation\*  $K_\lambda = \sum [p(n-1)] / \sum (pD_{tp})$ , where  $D_{tp}$  was taken alternatively from eq. (10) above and from Barrell and Sears' eq. (5.12). The 320 refractivity values were then recalculated by using corresponding values of  $K_\lambda$  and  $D_{tp}$ . From the residuals (obs.-calc.) thus obtained in the two cases one calculates a probable error of, respectively,

in the dashed curve. In this effect lies, apparently, the motivation for a density factor different from the theoretical value. However, the difference between the two curves is everywhere less than one unit in the last decimal place given for the observed refractivities, and it is small compared to the accidental fluctuations. It seems questionable, therefore, whether the parameters of the density factor can be determined from the refractivity measurements of BARRELL and SEARS with sufficient accuracy to prove a real deviation from the theoretical expression. Until such a deviation has been definitely established it seems preferable to accept the validity of the Lorenz-Lorentz equation. Then, from (10) and the relation

$$(n-1)_{tp} = (n-1)_s D_{tp}/D_s, \quad (11)$$

where  $D_s (= 720.775)$  is the density factor for standard air, we obtain for dry air in the temperature range 5 to 30 °C the general formula,

$$(n-1)_{tp} = \frac{p(n-1)_s}{720.775} \cdot \frac{1+p(0.817-0.0133t) \times 10^{-6}}{1+0.0036610t}, \quad (12)$$

where  $t$  is in °C,  $p$  in torr, and  $(n-1)_s$  is given by the dispersion formula for standard air.

By transforming the last factor in (12) and adopting a fixed value for  $p$  in the denominator, say  $p = 750$ , we get

$$D_{tp}/p = \frac{1+(a-bt)p}{1+\alpha t} \approx \frac{1+ap}{1+(\alpha+bp)t} = \frac{1+0.817 \times 10^{-6}p}{t+0.003671t}. \quad (13)$$

This gives the density factor in the more usual form. The  $n$ -values obtained with (13) differ from those of formula (12) by less than  $1.6 \times 10^{-8}$  over the range 0–800 torr and 5–30 °C. Around  $p = 700$  the results happen to be practically identical.

Table 5. Sums of residuals,  $(n_{\text{obs.}} - n_{\text{calc.}}) \times 10^6$ , obtained from Barrell and Sears' measurements at 8 different wavelengths when using a density factor according to equation (10) or (in parentheses) according to Barrell and Sears' equation (5.12)

$p$ (torr)	12 °C	16 °C	20 °C	25 °C	31 °C	Total
100	-9 (-6)	-2 (0)	-7 (-5)	-11 (-8)	-14 (-12)	-43 (-31)
200	-7 (-5)	-6 (+1)	0 (+7)	-14 (-9)	-15 (-11)	-42 (-17)
300	-17 (-12)	+2 (+7)	-8 (-3)	-17 (-10)	-25 (-17)	-65 (-35)
400	-4 (+2)	+13 (+19)	-11 (-7)	-8 (-3)	+8 (+12)	-2 (+23)
500	+2 (+3)	-8 (-4)	+7 (+11)	-8 (-3)	-30 (-25)	-37 (-18)
600	0 (-2)	+28 (+28)	+3 (+6)	-6 (-4)	+18 (+22)	+43 (+50)
700	+4 (-2)	+28 (+25)	-2 (-7)	+5 (+4)	+15 (+15)	+50 (+35)
800	-25 (-35)	+32 (+23)	0 (-8)	-8 (-12)	-8 (-12)	-9 (-44)
Total	-56 (-57)	+87 (+99)	-18 (-6)	-67 (-45)	-51 (-28)	-105 (-37)

$1.4_0 \times 10^{-8}$  and  $1.4_3 \times 10^{-8}$ , the small difference indicating that the BARRELL and SEARS density factor can be replaced by (10) without a significant change in the overall accuracy of representation.

A more informative comparison is shown in Fig. 2, where we have plotted the algebraic sums of the residuals for various groups of observations (see Tab. 5), divided by the number of observations. The dashed line corresponds to BARRELL and SEARS' density factor and the full line to formula (10). The curves having temperature as abscissa are seen to be essentially equivalent, but in the lower graph the full curve shows some trend with pressure which is largely suppressed

\* BARRELL and SEARS, in their calculation of  $K_\lambda$ , seem to have omitted the weighting factor  $p$ , which we believe should be included, though the result is not appreciably affected.

The range of atmospheric conditions normally found in a laboratory can be adequately covered with a much simpler formula. By choosing for  $ap$  in (13) a fixed value so as to exactly reproduce (12) at  $p = 750$  torr and  $t = 20$  °C we get

$$D_{tp}/p = 1.000599/(1 + 0.003671t), \quad (14)$$

and

$$(n-1)_{tp} = (n-1)_s \times 0.00138823 p/(1 + 0.003671t). \quad (15)$$

Formula (15) can be used in place of (12) from 15 to 30 °C and 700 to 800 torr with no deviation in  $n$  larger than  $1.0 \times 10^{-8}$ .

#### The effect of carbon dioxide and water vapour

When calculating the effects on the refractive index of air of small admixtures of other gases or vapours we can assume that the constituents contri-

bute to the refractivity in proportion to their fractional molar concentrations  $a_i$  so that the resulting refractivity will be  $\sum a_i (n - 1)_i$ , the refractivities  $(n - 1)_i$  being referred to some standard conditions. As the molar volumes of various gases are approximately equal, the concentrations  $a_i$  may be replaced by fractional parts by volume, and the latter may be assumed proportional to the partial pressures if the density factors are sufficiently similar.

For atmospheric air we need to consider only CO<sub>2</sub> and H<sub>2</sub>O as variable constituents.

Carbon dioxide

Standard air is defined as containing CO<sub>2</sub> to 0.0003 parts by volume, corresponding in the normal atmosphere to a partial pressure of 0.23 torr. As the refractivity of CO<sub>2</sub> is about 50% higher than that of air this CO<sub>2</sub>-content increases the refractivity over that of CO<sub>2</sub>-free air by approximately  $0.5 \times 0.0003 \times (n - 1)_s = 4.5 \times 10^{-8}$ . We note that this difference is within the uncertainty of our present knowledge of the absolute refractivity of air. Even if the CO<sub>2</sub>-content of laboratory air may exceed the normal amount by some hundred per cent the correction for CO<sub>2</sub> is always a small quantity.

The best information on the refractivity of CO<sub>2</sub> appears to be obtained from KOCH (1914) and the CUTHBERTSONS (1920), even though more recent investigations have been published. We have transferred their figures for 0 °C to 15 °C by using  $\alpha = 0.00371$  and have recalculated their refractivities for different wavelengths on the common basis of  $(n - 1) = 42676 \times 10^{-8}$  for 5462 Å at 15° and 760 torr. The results are plotted against  $\sigma$  in Fig. 3 in the form of  $r = (n_{CO_2} - n_s) / (n - 1)_s$ , where the subscript s refers to standard air. From the graph we obtain

$$r = (n_{CO_2} - n_s) / (n - 1)_s = 0.5291 + 0.00360 \sigma, \quad (16)$$

with  $\sigma$  expressed in  $\mu m^{-1}$ . As the density factor of CO<sub>2</sub> is not much different from that of air this ratio  $r$  can be taken as independent of  $t$  and  $p$ . Considering that the variation of  $r$  is

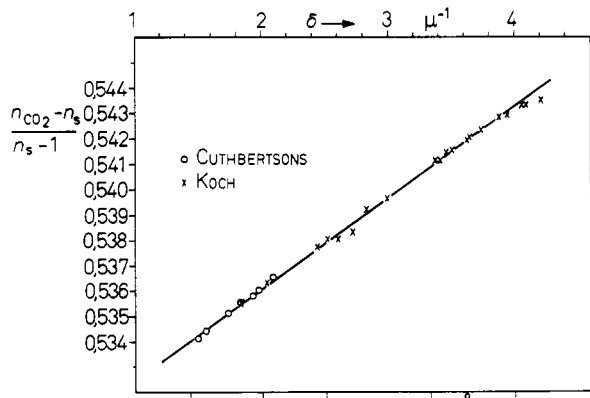


Fig. 3. Refractive index of carbon dioxide compared with that of air

within  $\pm 1\%$  over the wavelength range of interest, and that the CO<sub>2</sub>-correction always is a small quantity, we can for most purposes adopt a mean value of  $r$  as valid for all wavelengths. Then, for air containing  $x$  parts by volume of CO<sub>2</sub>,

$$(n - 1)_x = [1 + 0.540(x - 0.0003)](n - 1)_s. \quad (17)$$

This gives the factor 1.000162 which was used by EDLÉN (1953) for transferring  $(n - 1)$  for CO<sub>2</sub>-free air to standard air. The CO<sub>2</sub>-correction can also be given in the following form (cf. Fig. 4),

$$(n_{CO_2} - n_s) = (14485 + 117.8 \sigma^2) \times 10^{-8}, \quad (18)$$

which gives 0.1178 for the coefficient that MASUI (1957) gave as 0.11 in his formula.

Water vapour

The refractivity of water vapour is about 15% lower than that of air at equal  $t$  and  $p$ . As uncontrolled air often holds one to two per cent by volume of water vapour the refractivity may thus be changed by  $40$  to  $80 \times 10^{-8}$ , which is an order of magnitude more than the changes due to CO<sub>2</sub>. In the latter case the change in dispersion was found to be negligible, but this is not so for moist air.

BARRELL and SEARS (1939) determined the refractivity of water vapour by measuring the refractivity of moist air at  $p \approx 760$  torr and  $t \approx 30$  °C, with a partial pressure of water vapour of about 25 torr. Following BARRELL and SEARS we write the refractivity of air containing  $f$  torr of water vapour,

$$(n - 1)_{tpf} = \frac{K_\lambda (p - f) [1 + \beta'_t (p - f)]}{1 + \alpha t} + \frac{K'_\lambda f (1 + \beta'_t f)}{1 + \alpha t}, \quad (19)$$

where the primed quantities refer to water vapour, the unprimed to dry air, and  $\beta'_t = 27 \times 10^{-8}$  at a mean temperature

Table 6. Refractivity and dispersion of water vapour in comparison with air

$\lambda_{vac}$	(a) Erickson's relative refractivity	(b) (a) $\times 30.70$	(c) $(n - 1)_s \times 10^8$ $\times 0.00129382$	(c) - (b)	5.7224 - - 0.0457 $\sigma^2$
6440.25	0.981967	30.1464	35.7588	5.6124	5.6122
5462.27	0.989796	30.3867	35.9551	5.5684	5.5692
5087.24	0.994093	30.5187	36.0634	5.5447	5.5458
4801.25	0.998059	30.6404	36.1646	5.5242	5.5242
4679.46	1.000000	30.7000	36.2138	5.5138	5.5137
4359.56	1.005923	30.8818	36.3645	5.4827	5.4819
4047.71	1.013228	31.1061	36.5499	5.4438	5.4435
3611.54	1.027347	31.5396	36.9025	5.3629	5.3720

of 20 °C. By rearranging (19) and dropping the term in  $f^2 \beta'_t$  we obtain for the difference in refractive index of moist and dry air at equal temperature and total pressure

$$n_{tpf} - n_{tp} = -f \frac{K_\lambda (1 + 2 \beta'_t p) - K'_\lambda (1 + \beta'_t f)}{1 + \alpha t}. \quad (20)$$

From their measurements over the region 6440 - 4359 Å BARRELL and SEARS derived for  $K'_\lambda$  the expression

$$K'_\lambda = (31.59 + 0.2963 \sigma^2) \times 10^{-8}, \quad (21)$$

where  $\sigma$  is the wavenumber in  $\mu m^{-1}$ . The recent measurements by ERICKSON (1962) gave relative refractivities for water vapour with a much higher accuracy and covered the region

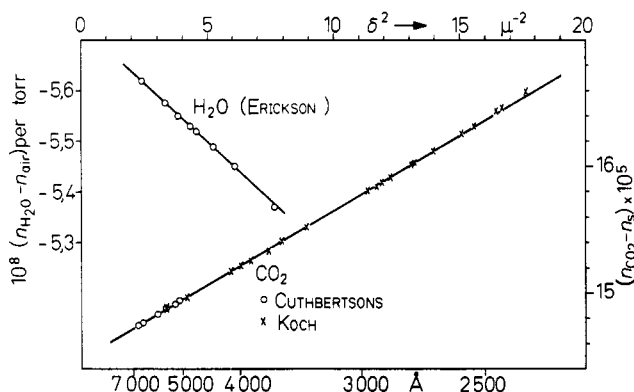


Fig. 4. Refractive index of water vapour and of carbon dioxide in comparison with that of air

6440 to 3611 Å. We shall, therefore, derive the water-vapour correction by normalizing ERICKSON's dispersion curve to BARRELL and SEARS' absolute values. For that purpose the last term in (19) is evaluated for  $f = 10$  torr and  $t = 20$  °C, and by taking  $K'_\lambda$  for  $\lambda = 4679.46$  Å from (21), which gives the value  $30.70 \times 10^{-8}$  for the refractivity per torr at these conditions. This value shows a satisfactory agreement with the CUTHBERTSONS' (1914) results for steam. ERICKSON's relative refractivities for different wavelengths (see Tab. 6) are now multiplied by  $30.70 \times 10^{-8}$ , and the result is subtracted from the corresponding values of  $K_\lambda (1 + 2 \beta'_t p) / (1 + \alpha t)$  obtained by multiplying the refractivity of standard air,  $(n - 1)_s$ , by 0.00129382. The coefficient of  $f$  in eq. (20) thus obtained is

plotted in Fig. 4 against  $\sigma^2$ . Over the region from 6440 to 4047 Å the points fall on a straight line with very small scatter (cf. Tab. 6). The point for 3611 Å, however, falls clearly below the line\*, which shows that the curve eventually bends downward in the ultraviolet. Until the ultraviolet region has been more extensively studied it seems preferable to restrict the equation to the visible region, where we find

$$n_{sp} - n_{sp} = -f(5.722_4 - 0.0457\sigma^2) \times 10^{-8} \quad (22)$$

for the difference in refractive index of moist air, holding  $f$  torr of water vapour, and dry air at the same total pressure  $p$ . The equation is valid for conditions not deviating too much from 20 °C,  $p = 760$  torr and  $f = 10$  torr.

In the expression for the correction to wavelengths measured in moist air, which was given by EDLÉN (1953) on the basis of BARRELL and SEARS' equation (7.7), the factor 0.63 should in accordance with (22) be changed to 0.457. Thus,

$$\Delta\lambda \times 10^5 = 0.457\lambda_2(\sigma_2^2 - \sigma_1^2)f, \quad (23)$$

where subscripts 1 and 2 refer to the reference line and the unknown line, respectively,  $\lambda$  and  $\sigma$  are given in  $\mu\text{m}$  and  $\mu\text{m}^{-1}$ , and  $\Delta\lambda$  is expressed in Å. The equation proposed by MASUI (1957) uses the coefficient 0.44, in close agreement with the present value 0.457.

\* I am obliged to Dr. ERICKSON for his kindness of verifying this deviation by rechecking the evaluation of his observations.

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## Platinum Resistance Thermometry in the Range 630—900 °C

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### Abstract

The performance of commercially produced, standard platinum resistance thermometers has been investigated in the region 630 – 900 °C. Particular attention was paid to resistance stability, quenching effects, and electrical insulation leakage. The limit of 900 °C was dictated by the use of mica insulation in these instruments.

The most serious problem encountered was that of insulation leakage at both high and low temperatures. The low temperature leakage was due to water that had been released from mica insulation when the thermometers were used at high temperatures, and this problem is studied in some detail here. A relationship between the magnitude of the galvanometer 'wet kick' and the insulation resistance has been established. The useful lifetime of the dry air filling in a thermometer has been estimated for various conditions of use.

Based on these studies, procedures have been recommended for stabilizing platinum resistance thermometers, annealing-out quenching effects, and reducing insulation leakage over this temperature range.

### Introduction

The standard platinum resistance thermometer is one of the most important practical devices for the measurement of temperature because of its extremely high precision, excellent reproducibility, and wide range of application. It is currently used, in conjunction with certain fixed points, to define the International Practical Temperature Scale (I.P.T.S.) of 1948 [1] over the range –183 to +630 °C. In addition, the extension of its range down to –260 °C and up to 1063 °C is now under consideration by the Comité Consultatif de Thermométrie. It is in connection with the extension towards 1063 °C that the present investigation was carried out.

A standard platinum resistance (s.p.r.) thermometer must conform to the specifications recommended in the 1960 edition of the I.P.T.S. 1948. It must have a platinum resistor that is fully annealed, mounted in a strain-free configuration, and of such purity that the resistance ratio  $R_{100}/R_0$  is  $> 1.3920$ .

Over the range 0 – 630.5 °C, the measured resistance  $R_t$  of the thermometer is related to the temperature  $t$  in degrees Celsius by the equation

$$R_t/R_0 = 1 + At + Bt^2 \quad (1)$$

where  $R_0$  is the resistance at the ice point (0 °C) and  $A$ ,  $B$  are constants determined by calibration at the steam point (100 °C) and either the sulphur point (444.6 °C) or zinc point (419.505 °C).

In earlier work (BERRY [2]) on the stability of commercially produced s.p.r. thermometers, it has been shown that prolonged use of these instruments in the region 400 – 630 °C causes the constants  $A$ ,  $B$ , and  $R_0$  to drift, necessitating periodic recalibrations. Although this instability becomes more pronounced as the operating temperature is increased, it is usually sufficiently slow, even at 630 °C, to permit temperature measurements to within 1 millidegree provided that the thermometer is recalibrated after 150 hours of use.

Further work on other silica-sheathed thermometers of commercial manufacture has confirmed the above result and has shown that reasonably good stability can be achieved even at temperatures up to 900 °C. The tests were not extended above this temperature because of the risk of permanently damaging the mica insulation by exfoliation. To determine