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Refractive Index Variations for Argon, Nitrogen, and Carbon Dioxide at $\lambda = 632.8$ nm (He−Ne Laser Light) in the Range 288.15 K $\leq T \leq$ 323.15 K, 0 < p < 110 kPa

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Direct measurements of the refractive index n of three gases (Ar, N_2, and CO_2) near ambient temperature and pressure states have been made by interferometry at the wavelength of the He−Ne laser light. Comparison with data obtained by interpolation of previous data shows good agreement ($\Delta(n - 1)/(n - 1) < 0.6\%$), the present data being always slightly higher than those obtained indirectly. Partial derivatives $\partial n/\partial T$, useful in interferogram interpretation, have also been obtained for the three gases.

Introduction

When interferometry is used to study heat transfer in a gas (Goldstein, 1983), it is necessary to know precisely how the refractive index n of this gas varies with pressure p and temperature T for the wavelength of the light used. Ideally, an analytical law of variation for n in terms of p and T is useful because such a law gives simply the partial derivatives of n necessary for interpretation of interferograms. If only small ranges of pressure and temperature are investigated, a local law can be used. For example, if the gas is at moderate pressure ($p < 10^5$ Pa) and temperature (288.15 K $\leq T \leq$ 323.15 K), we shall see later that it may be considered an ideal gas to a very close approximation. Consequently, using the Gladstone−Dale approximation of the Lorentz−Lorenz law, i.e., $(n - 1)/\rho = C$ (where ρ is the density of the gas and C a constant for the given wavelength) and the ideal gas equation $\rho = Mp/RT$ (where R is the constant of the ideal gas and M the molar weight), gives

$$n - 1 = \mu\frac{p}{T} \tag{1}$$

where μ is a constant.

For common gases such as air, more extended laws have been established (Barrel and Sears, 1940; Owens, 1967) but for others, like carbon dioxide, nitrogen, and argon (gases that are used in experimental simulations in our laboratory), little information is given in the literature. The only available data relative to He−Ne laser light have been calculated by Hauf and Grigull (1970) by interpolation from old data collected in the *International Critical Tables of Numerical Data* (1930) by means of Cauchy's formula:

$$n - 1 = \frac{A}{{\gamma_0}^2 - \gamma^2} \tag{2}$$

where the constants A and γ_0 are specific to each gas and γ is the frequency of the spectral line used.

In order to verify directly these data, we have measured, by interferometry, values of the μ constant for CO_2, N_2, and Ar, for the wavelength λ of the He−Ne laser ($\lambda = 632.8$ nm) in the vicinity of ambient temperature, and with pressure varying from vacuum to about normal atmospheric pressure. Then, we have computed $(n - 1)$ and $\partial n/\partial T$ for each gas at $p = 101.325$ kPa (760 mmHg) and $T = 293.15$ K (20 °C) in order to compare our experimental results with the interpolated data given by Hauf and Grigull (1970).

Table 1. Maximum Impurities Percentage for the Gases Used (in Volume, ppm)

	H_2O	C_nH_m	O_2	N_2	CO	H_2
Ar	3	1.5	3	10		
N_2	3	1.5	5			
CO_2	7	5	10	25	2	1

More recently, however, Obriot et al. (1993) have measured the refractive index of carbon dioxide with a Michelson interferometer and a He−Ne laser. But these measurements were performed at high pressure. Comparisons with Obriot's results have been made, but the two ranges of T and p have a very small common interval, and the accuracy of Obriot's data seems to be poorer than for our results. So we only compared our data with those published by Hauf and Grigull.

Experimental Section

Chemical Products. All gases used are from AIR LIQUIDE Co. France. The purity of each one is given in Table 1.

Instrumentation and Procedure. The measurements of n have been achieved with a classical Mach−Zender interferometer constructed at the LESETH. Figure 1 gives a diagram of the apparatus: two brass tubes of equal length L are immersed in a bath whose temperature is maintained at a fixed value T_i. These tubes, closed by glass windows are connected to a vacuum pump and to the gas holder. Temperature is measured by a K-type thermocouple connected to a COMARK (model 6600) electronic display. This system has been recently calibrated: deviations from a reference Pt probe are less than 0.2 K giving a relative accuracy of $\Delta T/T < 10^{-3}$ at ambient temperature.

Absolute pressure is measured by a calibrated electronic manometer whose linearity is better than 4×10^{-4} in the range $0 < p < 110$ kPa. Absolute values of pressure have

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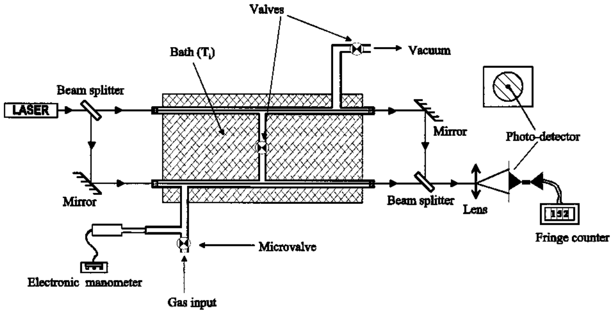

Figure 1. Diagram of the interferometer.

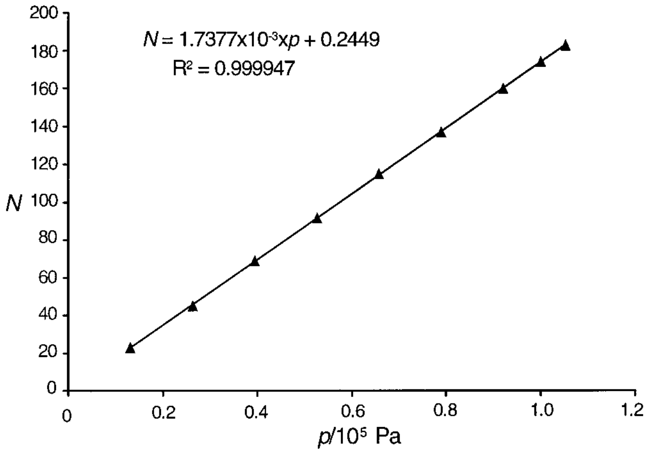

Figure 2. Example of $N = f(p)$ for nitrogen at $T_i = 298.15$ K.

been obtained by direct calibration with a SCHWIEN 140 absolute manometer.

The light source is a He–Ne laser (5 mW). Two beam splitters and two mirrors are used in order to separate and then to join the beams traveling in the two tubes.

Straight interference fringes are formed on a small diaphragm placed on a photodetector connected to an electronic fringe counter which gives the number N of bright fringes that have passed on the diaphragm since the initial state, where the two tubes were both vacuous to the present state where one pipe is still empty, the other being slowly filled with the gas by means of a microvalve. During this operation, the pressure rises from zero to 110 kPa. When N bright fringes have passed before the detector, the path length difference between the beams traveling in the two tubes is (Goldstein, 1983)

$$[n(p,T_i) - 1]L = N\lambda \qquad (T_i \text{ being the imposed constant temperature and } \lambda \text{ the wavelength})$$

From eq 1 we obtain

$$\mu\frac{p}{T_i} = \frac{N\lambda}{L} \quad \text{or} \quad N = \frac{\mu L}{\lambda T_i}p \tag{3}$$

Results

We can draw the graph of N versus p, which is, in theory, a straight line if the initial assumptions (the gas is ideal and the Gladstone–Dale law is valid) are valid. Figure 2 is an example of such a graph for nitrogen at $T_i = 298.15$ K (25 °C). In fact this graph follows very well a straight line with a regression coefficient very near unity ($R^2 = 0.9999$). The same behavior occurs with carbon dioxide and argon in the explored range. We can conclude that the initial assumptions are valid within the chosen range of T and p and therefore eq 3 can be used for the experimental determination of the constant μ.

Table 2. N as a Function of T_i and p for Nitrogen

15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
$p = 1.3170 \times 10^4$ Pa							
23	24	23	23	22	21	22	21
24	23	23	23	22	22	21	21
23	23	23	22	22	21	21	21
$p = 2.6340 \times 10^4$ Pa							
47	47	46	46	45	43	44	43
48	46	45	45	45	43	43	43
47	47	46	45	44	44	43	42
$p = 3.9509 \times 10^4$ Pa							
71	70	69	69	67	65	65	64
71	69	69	68	67	65	64	64
70	70	70	67	66	66	64	64
$p = 5.2679 \times 10^4$ Pa							
95	94	93	91	90	87	86	85
95	93	92	91	89	87	86	86
94	94	92	90	88	88	86	85
$p = 6.5848 \times 10^4$ Pa							
119	117	115	114	112	109	108	106
119	116	115	113	111	109	107	106
119	117	115	113	111	109	107	106
$p = 7.9018 \times 10^4$ Pa							
142	140	138	137	134	131	129	127
142	139	137	136	133	131	129	127
142	140	138	135	133	132	129	127
$p = 9.2187 \times 10^4$ Pa							
166	164	161	159	156	152	151	148
165	163	160	158	155	152	150	148
165	164	161	157	155	153	150	148
$p = 1.0009 \times 10^5$ Pa							
180	177	175	172	170	165	164	161
180	176	174	172	169	165	163	162
180	178	174	171	168	166	163	161
$p = 1.0536 \times 10^5$ Pa							
190	187	184	182	178	174	172	170
189	186	183	182	178	174	172	170
189	187	184	180	177	175	172	170

For each gas, we have chosen eight values of T_i from 15 °C to 50 °C. Three runs were made for each temperature T_i. For each run, we obtained a linear regression equation such as $N = \alpha p + \beta$. Theoretically, the β constant should be zero, because $(n - 1)$ tends to zero when p tends to zero. In fact, at the initial time (p near zero) the interference intensity on the diaphragm takes any value from minimum to maximum, just as when the pressure equals p. Therefore, in the worse case we may lose two bright fringes, one at the beginning, one at the end. So, N being only an integer, we can postulate that uncertainty ΔN of N is lower than 2 and that β can take a nonzero value. Fortunately, only α is relevant as far as μ determination is concerned.

Table 2, relative to nitrogen, shows that differences between the three experimental values of N for a given state of the gas is always $\Delta N < 2$. The same fact is observed for the other two gases.

Results relative to carbon dioxide and argon are given in Supporting Information.

To extract the most probable value of μ from our experiments, we have adopted the following procedure:

(1) Linear regression gives α, β, and the correlation coefficient R^2 for each run.

(2) Equation 3 is used to compute μ from α, T_i, L, and λ:

$$\mu = \lambda T_i \alpha / L \qquad (\text{with our apparatus } L = 40.64 \text{ cm at } 25\ °\text{C and } \lambda = 632.8 \text{ nm})$$

Table 3. Computation of μ from the 24 Runs for Nitrogen

$\alpha/(10^3\ \mathrm{Pa}^{-1})$	β	R^2	$\mu/(10^9\ \mathrm{K{\cdot}Pa}^{-1})$
1.8069	−0.500	0.999 975	810.70
1.7888	0.650	0.999 966	802.61
1.8029	−0.693	0.999 937	808.93
1.7681	0.531	0.999 968	807.06
1.7681	−0.469	0.999 968	807.06
1.7780	−0.102	0.999 977	811.58
1.7460	0.161	0.999 967	810.58
1.7377	0.024	0.999 947	806.72
1.7404	0.410	0.999 951	807.96
1.7182	0.713	0.999 955	811.04
1.7200	0.040	0.999 946	811.91
1.7113	−0.289	0.999 968	807.76
1.6924	0.246	0.999 948	812.05
1.6843	0.206	0.999 964	808.18
1.6838	−0.313	0.999 978	807.90
1.6576	−0.530	0.999 965	808.23
1.6518	−0.051	0.999 965	805.42
1.6631	−0.106	0.999 919	810.94
1.6282	0.675	0.999 967	806.60
1.6334	−0.324	0.999 978	809.18
1.6334	−0.324	0.999 978	809.18
1.6068	0.267	0.999 963	808.48
1.6096	0.306	0.999 897	809.92
1.6110	−0.117	0.999 967	810.63
	mean value of $\mu/(\mathrm{K{\cdot}Pa}^{-1})$	808.8×10^{-9}	
	confidence interval/$(\mathrm{K{\cdot}Pa}^{-1})$	1.2×10^{-9}	
	std dev/$(\mathrm{K{\cdot}Pa}^{-1})$	2.3×10^{-9}	

Table 4. Most Probable Values of the μ *Constant* for λ = 632.8 nm (in the Range (288.15 K ≤ T ≤ 323.15 K); (0 < p < 110 kPa))$\mu/(10^9\ \mathrm{K{\cdot}Pa}^{-1})$

Ar	762.0 ± 1.2
N_2	808.8 ± 1.2
CO_2	1211.1 ± 1.5

Table 5. Comparison of Refractive Indexes ($(n - 1) \times 10^6$)

	Ar	N_2	CO_2
Hauf and Grigull	261.8	278.1	417.4
our results	263.3 ± 0.8	279.5 ± 0.8	418.6 ± 1.1
rel diff (%)	+0.6	+0.5	+0.3

(3) Then the mean value of μ, the confidence interval, and the standard deviation are computed.

We can calculate the mean value of μ because, at moderate temperature and pressure, we have seen that three gases investigated could be considered as ideal gases. This means that the experimental value of μ is the result of more than 200 measurements.

Table 3 gives the results of this procedure for nitrogen.

Table 4 gives μ for the three gases computed by the same procedure.

Accuracy. From eq 1 we can write

$$\frac{\Delta(n-1)}{n-1} = \frac{\Delta\mu}{\mu} + \frac{\Delta p}{p} + \frac{\Delta T}{T} \tag{4}$$

with $\Delta\mu/\mu$ given by the confidence interval of μ, $\Delta p/p = 4 \times 10^{-4}$, $\Delta T/T = 10^{-3}$. The results of this calculation are indicated in Table 5.

Moreover, we note that the effect of the linear expansion of the tubes is irrelevant, being a second-order effect ($\Delta N < 1/10$).

Discussion

To compare our results with those of the literature, we have computed, on the basis of the obtained μ values, the refractive index of the three investigated gases for λ = 632.8 nm, T_i = 293.15 K, and p = 101.325 kPa (760 mmHg).

Table 6. Comparison of Refractivities ($r/(10^3\mathrm{m^3{\cdot}kg^{-1}})$)

	Ar	N_2	CO_2
$M/(10^3\ \mathrm{kg{\cdot}mol^{-1}})$	39.95	28.02	44.01
Hauf and Grigull	0.1052	0.1592	0.1521
our results	0.1057	0.1600	0.1525
rel diff (%)	+0.5	+0.5	+0.3

Table 7. Comparison of ($\partial n/\partial T$)($|(\partial n/\partial T)|/(10^6\ \mathrm{K}^{-1})$)

	Ar	N_2	CO_2
Hauf and Grigull	0.894	0.949	1.424
our results	0.898	0.953	1.428
rel diff (%)	+0.4	+0.4	+0.3

Table 5 gives our results compared with those of Hauf and Grigull (1970). We can see that discrepancies between these data never exceed 0.6%; our experimental results are always larger than the values obtained by interpolations.

Also, we can compare in Table 6 the refractivities r, defined by eq 5, for the three gases with those given by Hauf and Grigull (1970).

$$n - 1 = \frac{3}{2}\frac{rMp}{RT} \tag{5}$$

From the experimental values of μ, we have computed the first partial derivative $\partial n/\partial T$ at p = 101.325 kPa and T_i = 293.15 K from the equation:

$$\frac{\partial n}{\partial T} = -\mu\frac{p}{T^2} \tag{6}$$

Table 7 shows that our results agree very well with those of Hauf and Grigull (1970), computed on the basis of the *International Critical Table of Numerical Data* (1930).

Discrepancies observed between directly measured refractive indexes by means of the He−Ne laser source and calculated values based on spectral line measurements may be caused by differences in calibration of pressure and temperature measurements.

Supporting Information Available:

Tables of N as a function of T_i and p and computation of the constant μ for carbon dioxide and argon. This material is available free of charge via the Internet at http://pubs.acs.org.

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