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Optical Dispersion and Molar Refraction at Zero Frequency for Compressed Nitrogen, Argon, and Carbon Dioxide Measured as Functions of Density

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Data obtained by displacement interferometry have been reduced to give the variation of refractive index at infinite wave-length with density for pure nitrogen up to 0.01656 gram per cc. Precise data are also presented for dispersion in pure argon, and the Cauchy constants under NTP conditions are evaluated as follows for this gas: $A_0-1=0.0002771\pm0.0000008$, $B_0=1.477\times10^{-14}$. It is also noted that the Lorentz-Lorenz function, and hence the molar refraction at zero frequency, are independent of density for these two gases; the density range for argon extending up to 0.03342 gram per cc. The values of molar refraction are found to be 4.369 ± 0.003 cc for nitrogen and 4.138 ± 0.012 cc for argon. Preliminary work on carbon dioxide indicates a slight negative deviation from linearity for $(A-1)$ with density, and a marked negative variation of the Lorentz-Lorenz function with density. The latter means a decrease in the molar refraction at zero frequency, and suggests a decrease in the molar polarization with density. This is not in accord with the findings of Keyes and Oncley who report an increase of molar polarization with density for this gas. The NTP values of the Cauchy constants for CO_2 are also evaluated as follows: $(A_0-1)=0.0004419\pm0.0000036$, and $B_0=2.791\times10^{-14}$. The extrapolated value of the molar refraction at zero frequency is found to be approximately 6.65 cc.

INTRODUCTION

A PRECISE method for measuring the refractive index of a gas by displacement interferometry has been described by the writer in earlier papers.[1, 2] The present paper deals first with an analysis of data previously reported for purified nitrogen over a range of pressures from zero up to fourteen atmospheres.[2] The reduced data give the variation of refractive index at infinite wave-length with density, so that it is now possible to report with some degree of precision the behavior of the Lorentz-Lorenz function up to a density of 0.01656 gram per cc and to evaluate the molar refraction at zero frequency, or the molar polarization for this gas. The present paper also deals with a similar analysis for pure argon over a pressure range from zero to eighteen atmospheres, and presents some preliminary results for carbon dioxide observed over approximately the same pressure range.

This work was interrupted by the transfer of the apparatus to a new location,[3] which necessitated its complete reassembly with numerous alterations. The publication of earlier data was postponed until they could be confirmed in the new location. It is now gratifying to report that recent observations taken with the reassembled equipment are in complete agreement with the earlier data, and hence lend added significance to them. The complete analysis of the new CO_2 data, however, in which the density range is extended appreciably, will be presented later.

THEORY

If the refractive index of a gas is represented by a Cauchy expansion

$$\mu=A+B/\lambda^2+C/\lambda^4+\cdots, \qquad (1)$$

where A presumably represents the infinite wave-length value of the refractive index, the fundamental equation of the displacement interferometer is

$$\Delta x/e=(A-1)+3B/\lambda^2+5C/\lambda^4+\cdots, \qquad (2)$$

where Δx is the observable displacement of the fringe system, e is the length of the gas tube, and the other symbols have the same significance as in the Cauchy equation. It was shown in the earlier work that $A-1$ is linear with pressure for pure nitrogen and that only two constants A and B are necessary to describe the data up to the limiting pressures used, namely, 14.145 atmospheres. It was also shown that these two constants, reduced to NTP values and called A_0 and B_0, respectively, are as follows: for nitrogen $A_0-1=0.0002932$ to better than one-tenth of one percent, and $B_0=1.637\times10^{-14}$.

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[1] C. E. Bennett, Phys. Rev. **37**, 263 (1931).
[2] C. E. Bennett, Phys. Rev. **45**, 200 (1934).
[3] Former work done at the Massachusetts Institute of Technology.

Since, to a first approximation, pressure is proportional to density and $A-1$ is proportional to $(A^2-1)/(A^2+2)$, it was concluded that the above results constitute a rough check on the constancy of the Lorentz-Lorenz relation $(A^2-1)/(A^2+2)(1/\rho)$ in this pressure range, where ρ is the density. Also, since the refractive index measurements here reported are very accurately determined, the question of converting pressures to densities by an accurate equation of state is suggested to test the validity of this relation more precisely.

The density values reported in this paper are obtained by the use of the Keyes equation of state,[4] the constants for which are now available for several gases. This equation is usually expressed in terms of the pressure as follows:

$$p=\frac{RT}{v-\beta e^{-\alpha/v}}-\frac{A}{(v+l)^2}, \tag{3}$$

but it can be rearranged to express the specific volume (the reciprocal of density), in terms of pressure and temperature, thus

$$v=\frac{RT}{p}+\left(\beta-\frac{A}{RT}\right)-\left(\alpha\beta+\frac{2Al}{RT}\right)\frac{P}{RT}. \tag{4}$$

TABLE I. *Refractive index at zero frequency and the Lorentz-Lorenz relation as functions of density for pure nitrogen.*

ρ(g/cc)	p(cm Hg)	t°C	$A-1$	$\frac{1}{\rho}\frac{A^2-1}{A^2+2}$
0.0043061	309.75	50.0	0.0010127	0.15676
0.0045933	309.80	30.0	0.0010781	0.15645
0.0049116	331.22	30.0	0.0011541	0.15662
0.0052798	356.04	30.0	0.0012384	0.15633
0.0052904	321.09	00.0	0.0012333	0.15538
0.0072160	437.68	00.0	0.0016812	0.15528
0.0073795	497.49	30.0	0.0017282	0.15608
0.0081050	582.91	50.0	0.0019032	0.15650
0.0084055	566.56	30.0	0.0019664	0.15591
0.0084062	566.61	30.0	0.0019692	0.15612
0.0090645	549.42	00.0	0.0021146	0.15546
0.0092928	626.23	30.0	0.0021770	0.15612
0.010942	662.69	00.0	0.0025535	0.15551
0.011885	800.59	30.0	0.0027770	0.15570
0.011931	803.64	30.0	0.0027915	0.15591
0.013080	791.48	00.0	0.0030521	0.15548
0.014219	1022.20	50.0	0.0033389	0.15622
0.015977	1075.36	30.0	0.0037327	0.15565
0.016559	1000.57	00.0	0.0038584	0.15524
			MEAN	0.15596±0.00008
MOLAR REFRACTION $R_0=4.369\pm0.003$				

The values of $A-1$ at each density are readily calculated either by use of the precise value of B_0 properly adjusted for density and treated as a correction factor to $\Delta x/e$ by Eq. (2) rewritten thus

$$A-1=\Delta x/e-3B/\lambda^2, \tag{5}$$

or by a direct least-squares analysis of the individual values of $\Delta x/e$ at each of several wavelengths. In the latter method $(A-1)$ and B are determined simultaneously for each density observation. In the present work data for $\Delta x/e$ were available for each of the following wave-lengths: 5780A, 5461A, and 4359A, and calculations were made by both methods.

RESULTS

The results for nitrogen are listed in Table I, which shows the constancy of the Lorentz-Lorenz function up to a density of 0.01656 gram per cc. Attention is called to the fact that up to this density, at least, there is no observable variation of this function. The average value of the molar refraction at zero frequency is found to be 4.369±0.003 cc.

Table II contains hitherto unpublished data for pure argon. The refractive index and dispersion values are given for two different temperatures and six different pressures, reduced to density values by a Keyes equation of state as indicated above for nitrogen. The purity of the argon used was better than 99.8 percent as certified by the Air Reduction Company. It was also passed through the same purifying and drying system previously used for nitrogen.

The linearity of $(A-1)$ and B with density are clearly shown, as is also the constancy of the Lorentz-Lorenz function up to 0.033418 gram/cc. The values of A_0-1 and B_0 are found to be 0.0002771 ± 0.0000008, and 1.477×10^{-14}, respectively. The last column gives the values of molar refraction at zero frequency, or molar polarization and shows it to be independent of density with an average value of 4.138±0.012 cc.

PRELIMINARY WORK ON CARBON DIOXIDE

A limited amount of data on pure CO_2 at 50°C is presented in Table III. As in the case of argon, the values of $(A-1)$ and B were obtained by a least-squares analysis of the observations of $\Delta x/e$

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[4] F. G. Keyes, Proc. Nat. Acad. Sci. **3**, 323 (1917).

TABLE II. *Dispersion in pure argon as a function of density.*

No.	p cm Hg	t °C	ρ grams/cm³	$\Delta x/e$		
				5780A	5461A	4359A
1	305.63	00.00	0.0071834	0.0011684	0.0011750	0.0012057
2	573.20	30.00	0.012143	0.0019766	0.0019880	0.0020507
3	567.26	00.00	0.013372	0.0021815	0.0021932	0.0022529
4	1071.72	30.00	0.02275	0.0037168	0.0037359	0.0038450
5	1093.21	00.00	0.025916	0.0042235	0.0042449	0.0043693
6	1405.05	00.00	0.033418	0.0054422	0.0054699	0.0056398

No.	$A-1$	$B\times10^{14}$	$\frac{A-1}{\rho}$	$\frac{B}{\rho}\times10^{14}$	$\frac{A^2-1}{A^2+2}\frac{1}{\rho}$	R_0
1	0.0011199	5.438	0.15590	756.43	0.10391	4.1506
2	0.0018786	10.903	0.15470	897.84	0.10310	4.1182
3	0.0020877	10.465	0.15612	782.57	0.10405	4.1562
4	0.0035465	18.899	0.15572	829.83	0.10375	4.1442
5	0.0040295	21.513	0.15548	830.10	0.10359	4.1374
6	0.0051780	29.2319	0.15495	874.74	0.10321	4.1226
	MEAN		0.15548	828.58	0.10381	4.138±.012
	$A_0-1=0.0002771\pm0.0000008$				$B_0=1.4777\times10^{-14}$	

for each of three wave-lengths. In the case of CO_2 the deviations from the ideal gas law make it absolutely necessary for all pressures to be converted to densities before linearity considerations are even attempted. Here again, the Keyes equation of state was used. The observations were taken with the original apparatus for which the tube length e was 100.30 cm and the correction factor for the half-millimeter micrometer screw was 1.0104. The temperature was maintained constant to 0.01°C and pressure measurements were made with a Keyes type dead-weight gauge to approximately one millimeter of mercury over the entire range. The zero pressure reading was determined with a McLeod gauge to better than 10^{-2} mm Hg.

It is to be noted that although B is very nearly linear with density, $A-1$ deviates slightly. If one disregards for the moment this slight negative deviation, and considers the average values of $A-1$, and B, the following values of A_0-1, and B_0 are obtained by the use of standard density $\rho_0=0.0019769$: $A_0-1=0.0004419\pm0.0000036$, and $B_0=2.791\times10^{-14}$.

Incidentally, values of $\mu-1$ were also determined for several wave-lengths by Eq. (1), and the results were found to be in good agreement with those generally accepted. They are not listed here, however, since they are readily accessible in the literature.

Table III also shows the variation of the Lorentz-Lorenz function with density and the molar refraction at infinite wave-length for carbon dioxide. There appears to be a definite increase in molar refraction with density for this gas whereas this quantity seemed independent of density for nitrogen and argon. The molar refraction at zero frequency is found by extrapolation to be approximately 6.65 at zero density.

CONCLUSIONS

In view of these results it is concluded that the Lorentz-Lorenz function, and hence the molar refraction at zero frequency, are independent of density for pure nitrogen and argon over this density range, although Keyes and Oncley[5] find a slight increase in the molar polarization for nitrogen based upon dielectric constant measurements. The value of the molar refraction at zero frequency here obtained for nitrogen, however, is in good agreement with their value of molar polarization (4.37 cc), thus confirming the validity of the Maxwell law over this density range.

The results for argon represent a contribution to the rather limited amount of information available concerning the Lorentz-Lorenz function at high densities for the rare gases which are structurally quite simple. That this function

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[5] F. G. Keyes and J. L. Oncley, Chem. Rev. **19**, [3] 195 (1936).

TABLE III. *Dispersion in* CO_2 *as a function of density (data at 50°C)*

No.	p CM HG	MICROMETER READING 5780A	5461A	4359A	$\Delta x/e$ 5780A	5461A	4359A
0	0.0	00.5105	00.5790	00.9690	——	——	——
1	354.96	04.2500	04.3390	04.8500	0.0018835	0.0018939	0.0019548
2	426.61	05.0090	05.1050	05.6495	0.0022658	0.0022797	0.0023575
3	514.08	05.9565	06.0585	06.6285	0.0027431	0.0027600	0.0028506
4	612.54	07.0260	07.1345	07.7425	0.0032818	0.0033019	0.0034117
5	724.10	08.2410	08.3575	09.0180	0.0038938	0.0039180	0.0040542
6	846.31	09.5950	09.7260	10.4130	0.0045758	0.0046072	0.0047568
7	982.21	11.1395	11.2700	12.0415	0.0053537	0.0053849	0.0055771
8	1210.00	13.7780	13.9305	14.8160	0.0066827	0.0067250	0.0069746
9	1575.90	18.1455	18.3165	——	0.0088823	0.0089342	——

No.	ρ G/CC	$A-1$	$B\times10^{14}$	$\frac{A-1}{\rho}$	$\frac{B}{\rho}\times10^{14}$	$\left(\frac{A^2-1}{A^2+2}\right)\frac{1}{\rho}$	R_0
0	0.000000	——	——	——	——	——	——
1	0.0079023	0.0017886	10.529	0.22634	1332.4	0.15084	6.638
2	0.0095386	0.0021442	13.504	0.22479	1415.7	0.14981	6.593
3	0.011557	0.0026011	15.806	0.22507	1367.7	0.14998	6.601
4	0.013857	0.0031100	19.105	0.22443	1378.7	0.14955	6.582
5	0.016503	0.0036813	23.635	0.22307	1432.2	0.14862	6.541
6	0.019452	0.0043398	26.435	0.22310	1359.0	0.14863	6.541
7	0.022798	0.0050419	34.177	0.22115	1499.1	0.14731	6.483
8	0.028580	0.0062938	43.100	0.22021	1508.0	0.14665	6.454
9	0.038381	——	——	——	——	——	——
	$(A_0-1)=0.0004419\pm0.0000036$					$B_0=2.791\times10^{14}$	

would be constant for a monatomic gas is probably to be expected.

The negative variation of the Lorentz-Lorenz function with density for carbon dioxide, on the other hand, is also contrary to the findings of Keyes and Oncley who find a positive variation of the molar polarization. This point, however, is to be investigated further. Phillips[6] has reported such a negative variation although not so marked, but it is doubtful if the Phillips data are as accurate as that reported here over this density range. It may be that molar refraction at zero frequency is not the same as the molar polarization for carbon dioxide although Keyes and Oncley[5] show that the Phillips data, corrected for the effects of infra-red absorption bands, as suggested by Fuch,[7] yield a value for molar refraction nearly in agreement with the molar polarization. The agreement would be even better, however, on the basis of the results reported here.

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[6] P. Phillips, Proc. Roy. Soc. London **97A**, 225 (1920).

[7] O. Z. Fuch, Zeits. f. Physik **46**, 519 (1928).