NASA Technical Memorandum 80228

Gladestone-Dale Constant for CF_4

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MAY 1980

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Alpheus W. Burner, Jr., and William K. Goad
Langley Research Center
Hampton, Virginia

National Aeronautics
and Space Administration

Scientific and Technical
Information Office

1980

SUMMARY

The Gladstone-Dale constant, which relates refractive index to density, for CF_4 has been measured by counting fringes of a two-beam interferometer, one beam of which passes through a cell containing the test gas. The experimental approach and sources of systematic and imprecision errors are discussed. The constant for CF_4 was measured at several wavelengths in the visible region of the spectrum. A value of 0.122 cm^3/g with an uncertainty of ±0.001 cm^3/g was determined for use in the visible region. A procedure for noting the departure of the gas density from the ideal-gas law is discussed.

INTRODUCTION

In order to determine density flow fields in wind tunnels using interferometry, the constant relating refractive index to density for the particular test gas must be known. A relative error in the constant leads to a relative error of the same magnitude but of opposite sign in the density. This constant, referred to as the Gladstone-Dale constant, is readily available for a number of common test gases such as air and N_2 (ref. 1). For the unique test gas CF_4, for which refractive-index data are not available, the constant can be estimated from the atomic refractivities of carbon and flourine (ref. 2). This estimation can be verified using a two-beam interferometer to determine experimentally the Gladstone-Dale constant, the specific application being for holographic interferometric measurements made at the Langley Hypersonic CF_4 Tunnel (ref. 3).

SYMBOLS

a	mass fraction
K	Gladstone-Dale constant, cm^3/g
ℓ	inside cell length, cm
M	fringe shift
M_o	molecular weight
m	slope of fringe-shift/pressure curve
n	refractive index
n_o	reference refractive index
P	pressure, N/m^2
R	gas constant, J/kmol-K

s	path of light ray
T	absolute temperature, K
ρ	mass density, kg/m^3
ρ_o	reference mass density, kg/m^3
λ	vacuum wavelength, m

THEORY

The basic equation of interferometry is

$$M = \frac{1}{\lambda} \int_s [n(s) - n_o] \, ds \tag{1}$$

where M is the fringe shift, λ is the vacuum wavelength, s is the path of the light ray, $n(s)$ is the refractive index to be measured along the path s, and n_o is the reference refractive index. In order to relate the measured fringe shift to density (e.g., to obtain density fields in wind-tunnel flows), the relation between density and refractive index must be known. For gases in which the refractive index is close to unity, this relation is very closely approximated by

$$n - 1 = K\rho \tag{2}$$

where K is the specific refractivity, known as the Gladstone-Dale constant. The Gladstone-Dale constant (ref. 1) is dependent on the test gas and weakly dependent on wavelength and temperature.

If the test gas of interest is in a cell of length ℓ and the refractive index (and hence density) is constant along the path of the light ray, then equation (1) reduces to

$$M = \frac{2K\ell}{\lambda}(\rho - \rho_o) \tag{3}$$

for a double-pass interferometer. Thus K can be determined by measuring the fringe shift as the density is changed from ρ_o to ρ in a manner similar to the measurement of refractive index.

EXPERIMENTAL APPROACH

A Twyman-Green interferometer with laser light source was used to measure the Gladstone-Dale constant (fig. 1). One beam of the two-beam interferometer passed through an optical cell of inside length equal to 27.86 cm which could be evacuated to 10 N/m^2 and then slowly filled with the test gas to a pressure of 2×10^5 N/m^2 ($\approx$2 atm). A photodiode recorded on a strip chart the fringe shift caused by the change in density of the gas. The rate of fill of the test gas was controlled so that the fringes shifted at a rate of 1/2 to 1 fringe per second. The pressure of the test cell was measured and recorded approximately every 20 fringe peaks by a quartz-crystal pressure transducer. The output of the transducer was linearized by a microprocessor-based display unit to provide pressure indications with a repeatability of 3.4 N/m^2 and an overall uncertainty of 140 N/m^2 according to the manufacturer and verified by calibration. The temperature of the cell was measured with an iron-constantan (type J) thermocouple and recorded at the start, midpoint, and end of the scans. The resolution and overall uncertainty of the thermocouple and display unit were 0.05 and 0.5 K, respectively, according to the manufacturer and verified by calibration.

The densities corresponding to the fringe peaks were calculated from the measured temperatures and pressures using the real-gas equation of state for CF_4 (ref. 4). The slope (Gladstone-Dale constant) of fringe shift as a function of $2\ell\rho/\lambda$ was then determined by the method of least squares with equal weighting of the data. The correlation coefficient, which indicates the "goodness of fit" of the data to a linear model, and the standard deviation of the slope were computed. Since it is the slope of the curve which is to be measured, the fringe count is started on any convenient fringe peak at the low pressure of the scan. Thus what is plotted is the relative fringe count against $2\ell\rho/\lambda$ and the data may have a y-intercept which is nonzero.

RESULTS AND DISCUSSION

The results from three scans made of CF_4 from 10 N/m^2 to 2×10^5 N/m^2 at the He-Ne laser wavelength of 633 nm are presented in table I. The cell temperature during the three scans was 302 K. The mean of the slopes K was 0.1223 cm^3/g, which is 1 percent less than the value estimated from the atomic refractivities of carbon and fluorine (ref. 2). A plot of fringe-shift residuals as a function of $2\ell\rho/\lambda$ for one of the scans is shown in figure 2. If the Gladstone-Dale constant is known the refractive index can be calculated at a given temperature and pressure by computing the density and then applying equation (2). For instance, the refractive index of CF_4 at 293 K and 1 atm at 633 nm is computed from K to be 1.000448.

Measurements of the Gladstone-Dale constant of CF_4 were also made at four additional wavelengths at 303 K. Three of the wavelengths (458, 488, and 515 nm) were obtained from an argon ion laser. The fourth wavelength (816 nm) was obtained from a room-temperature continuous-wave laser diode. Three scans were made of each of the argon laser wavelengths. The mean slopes K for 458, 488, and 515 nm were, respectively, 0.1226, 0.1227, and 0.1220 cm^3/g with a maximum variation between values of K of 0.00054 cm^3/g for a particular wavelength.

For a single scan made at 816 nm, K was measured to be 0.1215 cm^3/g with a standard deviation of 0.00003 cm^3/g. Note that the maximum variation between K for the various wavelengths is 0.0012 cm^3/g, which is approximately 1 percent of K.

In order to verify the correctness of the experimental approach the Gladstone-Dale constants of 10 gases with known constants were measured at 633 nm. For these gases the density was calculated using the ideal-gas law

$$\rho = \frac{PM_o}{RT} \tag{4}$$

where P is pressure, R is the gas constant, and T is the absolute temperature. The slope and standard deviation of the slope of fringe shift as a function of pressure as determined by the method of least squares were multiplied by $\lambda RT/2\ell M_o$ to find the Gladstone-Dale constant and its standard deviation. A comparison of the measured and accepted values of the Gladstone-Dale constants from references 1 and 5 for the 10 gases is given in table II. Note that the weak temperature and wavelength dependence of the Gladstone-Dale constant makes such a comparison at slightly different wavelengths and temperatures meaningful.

For further verification of the experimental approach, the Gladstone-Dale constants were measured for three gases for which the constants were also computed by summing the atomic refractivities. The results for scans made from 10 N/m^2 to 10^5 N/m^2 are presented in table III. For one of the gases (C_2F_6) both real-gas (ref. 6) and ideal-gas densities were used in the computation of K. For C_2F_6 the real-gas density is 1.1 percent greater than the ideal-gas density at 10^5 N/m^2 and 300 K. The real-gas calculation of K was less than the ideal-gas calculation of K by 1.1 percent. The standard deviation of K for the real-gas calculation was half the standard deviation using ideal-gas densities to compute K and the correlation coefficient was closer to 1, indicating a better fit to the linear model.

A comparison of fringe-shift residuals, the measured fringe shift minus the fringe shift computed from the least-squares coefficients, as a function of pressure for the real- and ideal-gas calculations of K is presented in figure 3. Note that the plot of fringe-shift residuals using the ideal-gas density has a definite bow, whereas the plot of residuals using the real-gas density oscillates back and forth across the zero residual line as the pressure is increased. The bow for the residuals of the ideal-gas calculation of K is due to the pairing of density values less than the actual density values with the measured fringe-shift data. Figure 4 presents an exaggerated sketch of fringe-shift as a function of density for a gas in which the real-gas density is greater than the ideal-gas density over the range of pressures and at the temperature considered. A linear least-squares fit to the ideal-gas density curve would give a larger slope than the linear least-squares fit to the real-gas density curve. Also, the residuals would be positive at the lower and upper pressures and negative at the middle pressures, just as the C_2F_6 ideal-gas residuals show. If the real-gas densities are less than the ideal-gas densities over the pressure range considered, the residuals would be negative at the upper and lower pressures and positive at the middle pressures. For a gas such as N_2, for which the ideal- and real-gas densities differ only by 0.05 percent at 2×10^5 N/m^2 and 300 K (ref. 7), the plot of fringe-shift residuals against pressure does not have the bow (fig. 5). Thus the bow in the fringe-shift-residual plot when a gas is treated as ideal is a measure of the departure of the gas density from the ideal-gas law. An increase in the bow of the residual plot when using real-gas densities to compute K would indicate that the real-gas correction was of the wrong sign. If the bow is still relatively large but of opposite sign when K is computed using real-gas densities, then the real-gas correction would be of the correct sign, but too large.

STATEMENT OF UNCERTAINTY

The uncertainty of determining the Gladstone-Dale constant consists of both systematic and imprecision errors. The systematic errors are those errors which in repeated measurements do not change. The imprecision errors vary with repeated measurements and are statistically described by the standard deviation, which can be estimated by calculation with a limited sample.

Systematic Errors

For CF_4 at 300 K and 2×10^5 N/m^2 the real-gas correction is 0.7 percent of the ideal-gas density, so that the expression

$$K = \frac{\lambda RT}{2\ell M_o} m \tag{5}$$

where m is the slope of the fringe-shift/pressure curve, can be used for estimating the uncertainty of the measurement. The systematic error is estimated by multiplying K by the root-sum-square of the fractional systematic errors of the various parameters used to compute K in equation (5). The systematic errors due to the wavelength, gas constant, and molecular weight are negligible when compared with the temperature, cell-length, and slope systematic errors. According to the manufacturer the uncertainty in the temperature measuring system is 0.5 K, giving a fractional systematic error of 0.0017 for a temperature of 300 K. The inside cell length was determined by measuring the outside length and both window thicknesses with a micrometer caliper which had a resolution of 0.003 cm. Repeatability of the readings was 0.007 cm. The window thicknesses were then subtracted from the outside length to find the inside cell length. Taking the root-sum-square of the repeatability of the three length measurements and dividing by the inside cell length of 27.86 cm gives an estimate of the fractional systematic error for the cell length of 0.00044.

Systematic error in the slope measurement would occur if the pressure indications were, for example, high at the low-pressure end and linearly decreasing to a lower-than-true value at the high-pressure end. Taking as a worst case an error of twice the uncertainty in the pressure measurement, or 280 N/m^2 over 2 atm, the fractional systematic error in slope due to the pressure measurement would be 0.0013. Another source of systematic error for the slope would occur if the gas sampled had impurities. The Gladstone-Dale constant for a mixture of gases is given by

$$K = \sum K_i a_i \tag{6}$$

where K_i and a_i are the Gladstone-Dale constants and mass fractions for the various gases making up the mixture. For example, if the sample of CF_4 consisted of 99.7 percent CF_4 and 0.3 percent N_2 in mole percent, K for the mixture would be 0.09 percent larger than K for CF_4. The effective molecular weight of the mixture would be 0.2 percent smaller than the molecular weight of CF_4. The combined effects of a larger K and smaller effective molecular weight would cause the slope of M as a function of P for the mixture to be less than for CF_4 alone by 0.12 percent. The fractional systematic error from this source is arbitrarily taken to be 0.001. (The purity in mole percent of the sample of CF_4 tested was greater than 99 percent according to the supplier.)

Variations in ambient temperature and pressure can also cause systematic errors in the slope. During the period the Gladstone-Dale measurements were made the barometric pressure varied by as much as 0.03 percent during the 15 to 20 minutes for a single scan. If the ambient pressure decreased by 0.03 percent and the ambient temperature increased by 0.2 K, a typical excursion range of temperature during a single scan from 0 to 2 atm, the change in ambient density would be sensed by the interferometer as an additional fringe shift of 0.16, which would cause a slope fractional error of 0.00021. Taking the root-sum-square of the temperature, cell-length, and slope fractional systematic errors and multiplying by K gives ± 0.00029 cm^3/g as an estimate of the systematic error of the measurement process.

Imprecision Errors

The random variations in the determination of a fringe peak to initiate a pressure reading introduces imprecision error. The 3-per-second sampling rate of the signal processor and display unit for the pressure transducer also introduces imprecision error, since the time between the sampling of the pressure readings and the occurrence of the fringe peaks can vary by as much as 1/3 fringe for a fringe counting rate of 1 fringe per second. If this time between pressure reading and fringe peak were constant throughout the scan, then only the y-intercept would be affected, not the slope. Short-term variations in the ambient temperature and pressure as well as short-term spurious fringe shifts due to interferometer drift would introduce imprecision errors for a single scan. Variations in the rate of change of the ambient temperature and pressure and interferometer fringe-shift drift would lead to imprecision errors from scan to scan. The combined effect of the various imprecision errors is estimated from the computed standard deviation. Typical deviations for single scans consisting of 35 data points were ±0.00002 cm^3/g. The standard deviation of K computed from several scans was typically about 10 times larger than the standard deviation for K from a single scan. Six scans were made of CF_4 from 10 to 4×10^4 N/m^2. The standard deviation of the Gladstone-Dale constants calculated from the six scans was 0.00023 cm^3/g. Multiplying this standard deviation by the Student's t-value of 2.6 for a 95-percent confidence interval with 5 degrees of freedom gives ±0.00006 cm^3/g as an estimate of the imprecision error. Summing the systematic and imprecision errors gives ±0.0009 cm^3/g as an estimate of the uncertainty of the measurement process. Due to the very weak dispersion of K for CF_4, a value of 0.122 ± 0.001 cm^3/g for the Gladstone-Dale constant of CF_4 is recommended for use in the visible region of the spectrum.

CONCLUDING REMARKS

A two-beam laser interferometer has been used to measure the Gladstone-Dale constant of CF_4. The experimental approach and sources of error in the measurement have been discussed. The effects of departure from the ideal-gas law on the experiment have been described. The Gladstone-Dale constant of CF_4 was found to be very weakly dispersive, so that a value of 0.122 ± 0.001 cm^3/g is recommended for use in the visible region of the spectrum.

Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665
April 1, 1980

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TABLE I.- MEASURED VALUES OF GLADSTONE-DALE CONSTANT OF CF_4 AT 302 K AND 633 nm

Number of data points	Measured Gladstone-Dale constant, cm^3/g	Standard deviation, cm^3/g	Correlation coefficient
42	0.1221	0.000022	0.99999937
42	.1223	.000029	.99999935
35	.1224	.000016	.99999972

TABLE II.- COMPARISION OF MEASURED[a] AND ACCEPTED[b] VALUES

OF GLADSTONE-DALE CONSTANTS

Gas	Measured Gladstone-Dale constant, cm^3/g	Standard deviation, cm^3/g	Correlation coefficient	Accepted Gladstone-Dale constant, cm^3/g	Difference between measured and accepted values, percent
H_2	1.538	0.0010	0.9999981	1.54	-0.13
He	.1928	.00048	.9999672	.196	-1.6
Ne	.0740	.000097	.9999931	.074	0
N_2	.2378	.000083	.9999985	.238	-.08
Air	.2248	.00012	.9999980	.226	-.53
O_2	.1887	.00021	.9999928	.190	-.68
Ar	.1567	.000074	.9999989	.159	-1.4
CO_2	.2259	.00019	.9999968	.229	-1.4
Kr	.1135	.00012	.9999942	.114	-.44
Xe	.1174	.000089	.9999922	.119	-1.3

[a] At 300 K and 633 nm.
[b] From references 1 and 5 at 273 K and 589 nm.

TABLE III.- COMPARISON OF MEASURED[a] AND COMPUTED[b] VALUES

OF GLADSTONE-DALE CONSTANTS

Gas	Measured Gladstone-Dale constant, cm^3/g	Standard deviation, cm^3/g	Correlation coefficient	Computed Gladstone-Dale constant, cm^3/g	Difference between measured and computed values, percent
$CHClF_2$	0.2063	0.00025	0.999988	0.2047	0.78
CCl_2F_2	.2092	.00024	.999982	.2061	1.50
C_2F_6	.1329	.00010	.999994	.1321	.61

[a] At 300 K and 633 nm.
[b] Computed from atomic refractivities of C, H, Cl, and F taken from reference 2 at 293 K and 589 nm.

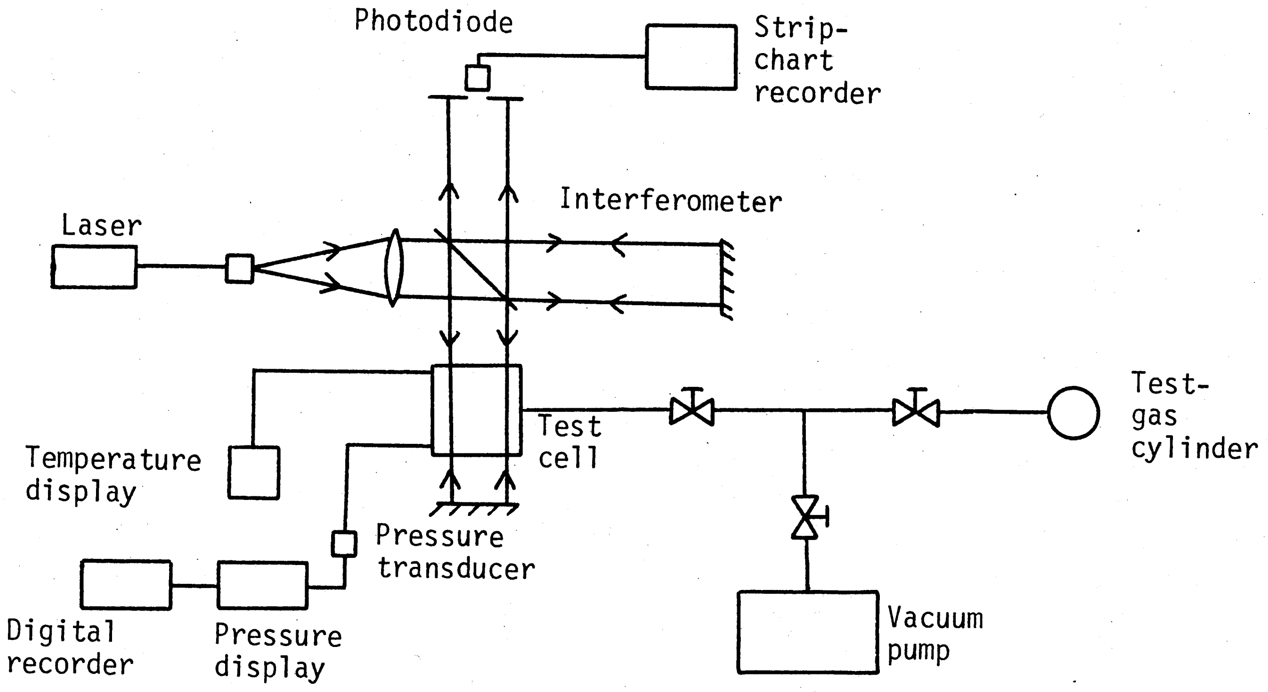


Figure 1.- Experimental setup used to measure Gladstone-Dale constants.

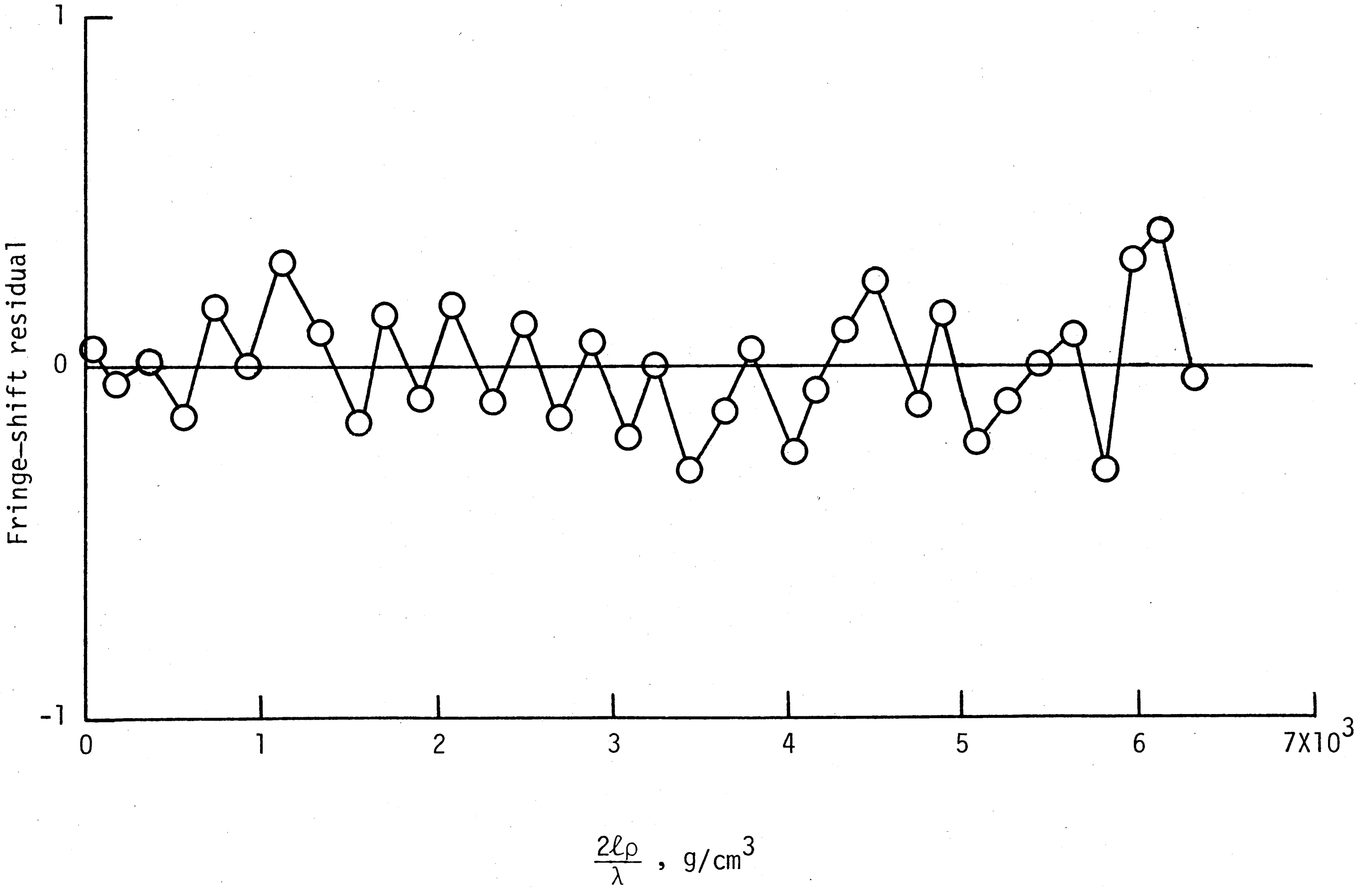
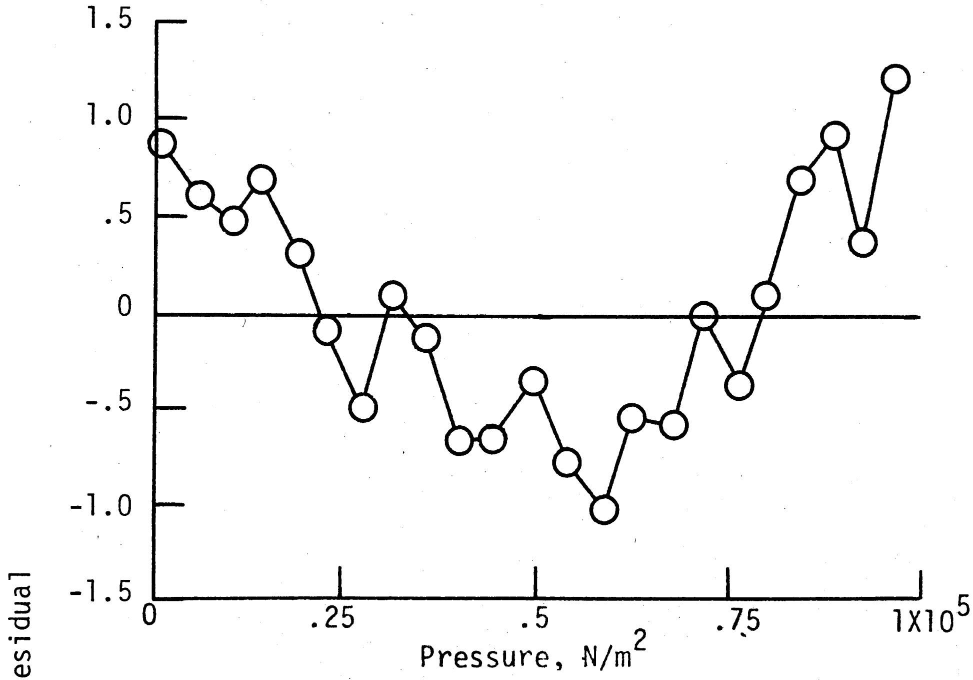
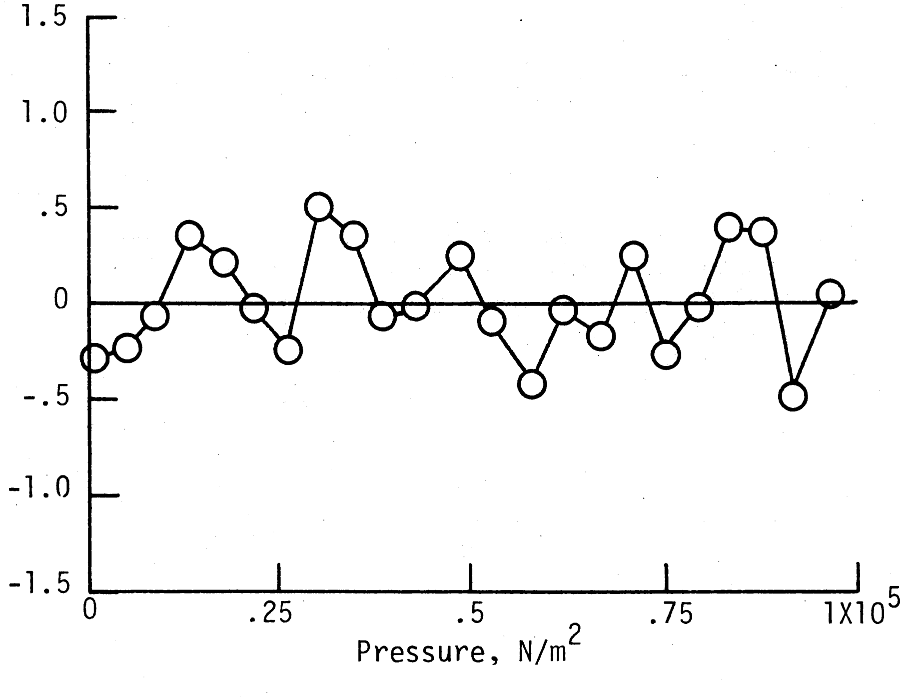


Figure 2.- Plot of fringe-shift residuals as a function of $2\ell\rho/\lambda$ for one of the CF_4 scans at 633 nm.



(a) Using ideal-gas densities to compute K.



(b) Using real-gas densities to compute K.

Figure 3.- Comparison of fringe-shift residuals for C_2F_6 using ideal- and real-gas densities in the computation of K.

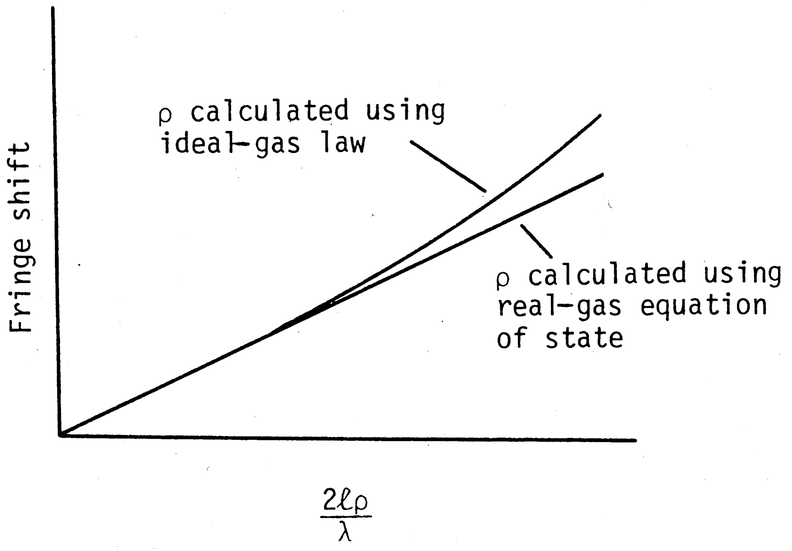


Figure 4.- Exaggerated plot of fringe shift as a function of $2\ell\rho/\lambda$ for a gas with ρ calculated using both ideal-gas law and real-gas equation of state.

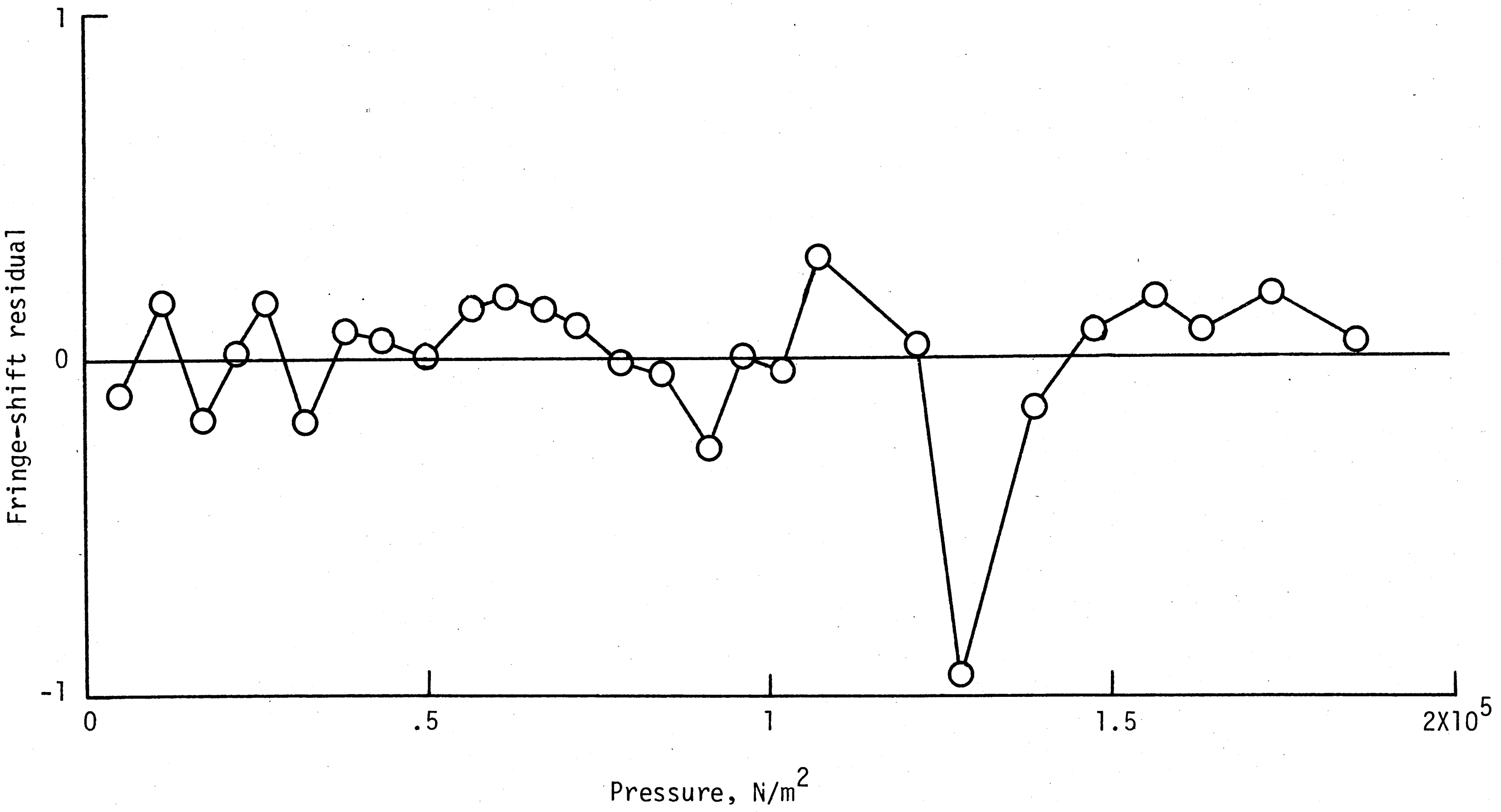


Figure 5.- Fringe-shift residual as a function of pressure for N_2 treated as an ideal gas.

1. Report No. NASA TM-80228	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle GLADSTONE-DALE CONSTANT FOR CF_4	5. Report Date May 1980
	6. Performing Organization Code
7. Author(s) Alpheus W. Burner, Jr., and William K. Goad	8. Performing Organization Report No. L-13551
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665	10. Work Unit No. 506-51-23-02
	11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546	13. Type of Report and Period Covered Technical Memorandum
	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words (Suggested by Author(s)) Gladstone-Dale constant Refractive index Interferometer	18. Distribution Statement Unclassified - Unlimited Subject Category 74

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 15	22. Price* $4.00

* For sale by the National Technical Information Service, Springfield, Virginia 22161