Refraction Index and Dielectric Constant for Freon-13

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COUNTING experiments at the Bevatron frequency require a counter that distinguishes particles by velocity selection in a momentum-analyzed beam. The critical velocity is often in the region of $\beta = 0.9$. Particles can be selected on the basis of their production of Cerenkov radiation in a medium whose index of refraction is 1.1.

A physical chemistry rule states that the index of refraction of materials at their critical points is 1.126 (*9*). Although this rule does not hold precisely, the properties of materials in the region of their critical points is such that indices in the range of 1.05 to 1.15 are not obtainable at temperatures and pressures greatly below the critical temperature and pressure of the material.

If a counter can be designed that uses a material at temperatures above its critical temperature, the index of refraction can be varied continuously from unity to some limit determined by the upper limit of pressure that can be held by the container for the material. There are very few materials with critical temperatures close to ordinary room temperatures and with reasonably low critical pressures.

Chlorotrifluoromethane (Freon-13) is exceptional in its desirable properties (Table I). It is nontoxic, noncorrosive, nonflammable, and available commercially in almost unlimited quantities at very high purity. The thermodynamic properties have been thoroughly investigated by Albright and Martin (*1*).

The liquid is completely colorless, even in large thickness. A spectrophotometric measurement of 2 inches of the liquid indicated a transmission of more than 0.25 even at 2100 A. (short wave limit of the apparatus). Unevaluated refraction effects on this measurement make the results consistent with complete transparency, at wave lengths from 2100 to 8000 A.

In the course of considering this material for counter use, the index of refraction and the dielectric constant were measured as functions of the density of the material. Both are similar functions of density, and the dielectric constant can be measured remotely to indicate the index of refraction of the counter material during use of the counter.

Table I. Properties of Chlorotrifluoromethane (*4*)

Chemical formula	$CClF_3$
Molecular weight	104.47
Critical temperatures	28.9° C. (83.9° F.)
Critical pressure	38.2 Atm. (561 p.s.i.)
Critical density	0.578 G./cc.
Flammability	Nonflammable
Toxicity	Probably group 6[a]
Stability	Stable up to at least 300° F. in the presence of oil, steel, and copper.

[a] Gases or vapors that, in concentration up to at least 20% by volume, do not appear to produce injury in exposure of the order of 2 hours.

The index of refraction, n, for fluids follows the Lorenz-Lorentz law (*3*), which predicts n to be a single-valued function of the density, ρ, of the material—governed by the molar refractivity, R, and the molecular weight, M. The low-frequency dielectric constant, ϵ, follows a similar Clausius-Mosotti law (*8*) which includes a term dependent on the electric dipole moment of the molecule, μ (usually measured in Debye units of 10^{-18} statcoulomb-cm.), and the absolute temperature, T. (N is Avogardro's number and k is Boltzman's constant.) Thus

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} = R$$

and

$$\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{M}{\rho} = R + \frac{4\pi N}{9k}\,\frac{\mu^2}{T}$$

From these two relations, one can derive the following approximate relation:

$$(\epsilon - 1) \approx 2\Gamma(n-1) + \tfrac{1}{3}[4\Gamma^2 - \Gamma](n-1)^2,$$

where

$$\Gamma = 1 + \frac{4\pi N}{9k}\left(\frac{\mu^2}{TR}\right)$$

APPARATUS

The experimental arrangement is shown schematically in Figure 1. The gas transfer between the storage container and the experimental vessel was effected by heating or cooling the storage container. The experimental vessel was temperature controlled.

Mass of the material transferred was measured by weighing the storage container. The density in the experimental vessel was obtained by dividing the volume into the mass transferred.

The 1000-cycle dielectric constant was determined from the capacity between a series of plates in the chamber, after subtracting the capacity of leads, etc. The ratio of the capacity with the material in the chamber to that with the chamber evacuated is the dielectric constant.

Index of refraction at 5461 A. was measured by counting fringe shifts in a Fabry-Perot etalon (2.51 mm. spacing) mounted inside the chamber—starting from vacuum conditions. The line was isolated from the mercury-arc spectrum by filters, and was sufficiently monochromatic for this application (*2*). The fringe counting was aided by measuring the light intensity of the central fringe with a photoelectric cell, then recording the measurement *vs.* time on a strip-chart recorder.

PROCEDURE

Freon-13 was slowly introduced into the evacuated chamber, and periodic measurements of the storage container weight and the capacitance were recorded at appropriate points on the chart recording the fringe shifts. After the chamber was filled to the maximum density attainable, the Freon was slowly returned to the storage container, and periodic measurements were recorded again.

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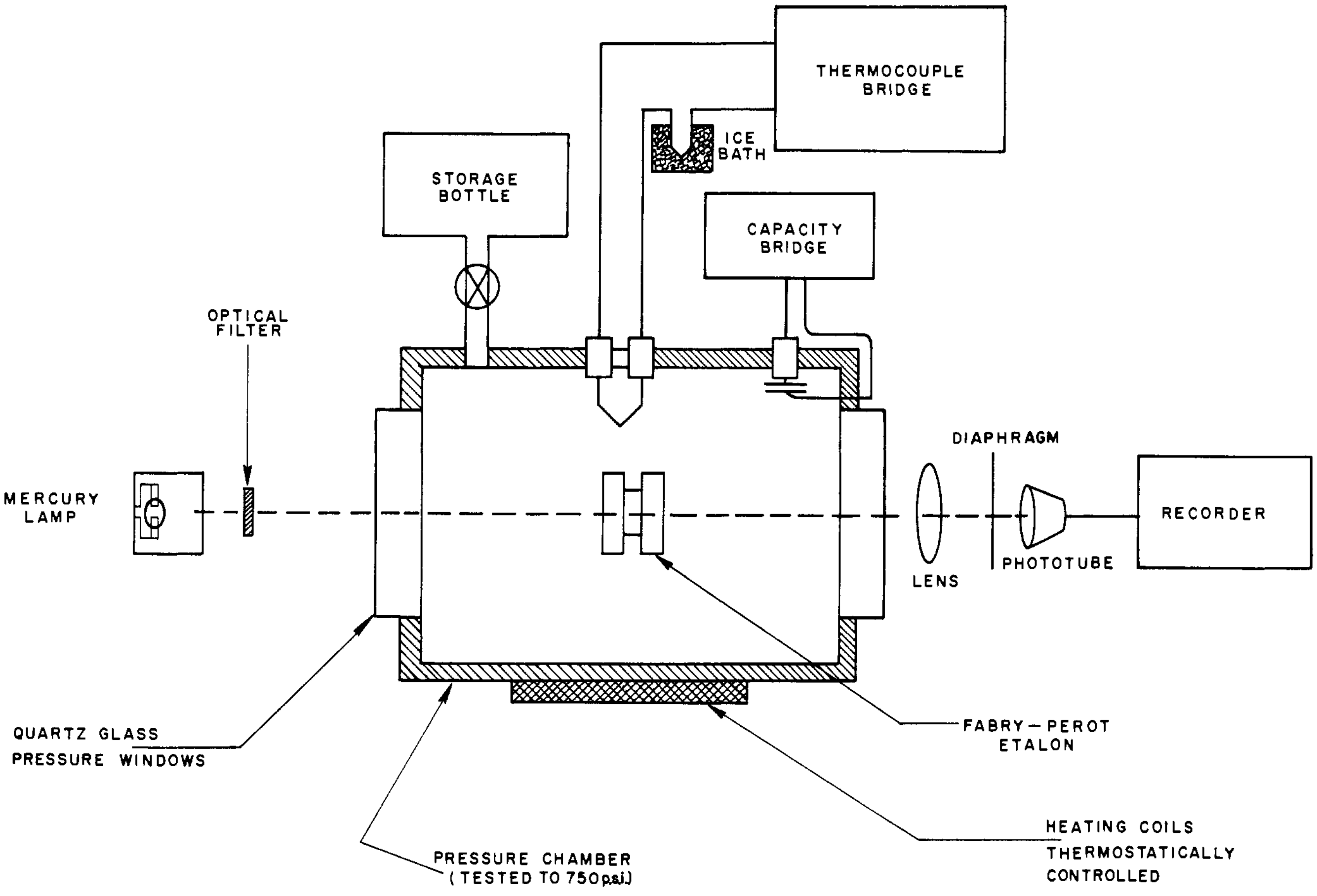

Figure 1. Schematic diagram of experimental arrangement

The temperature of the chamber was held near 90° F. Great care had to be taken to make the procedure slow enough. Since the material was very close to its critical point, the density at a given pressure was a very steep function of the temperature. Minor temperature inequalities in such a material produce great density and refractive-index inequalities that give rise to turbulence and shimmer, which spoil fringe counting.

RESULTS

The relationships between the density, dielectric constant, and refractive index are shown in Figures 2, 3, and 4. In these graphs the experimental points appear to wander from simple predicted curves by approximately 0.007 in density, 0.006 in dielectric constant, and 0.008 in refractive index. Each curve can be fitted by adjusting a single parameter, and the best fitting parameters are

$$R = 12.7 \pm 0.1 \text{ cc./g. mole}$$

$$R + \frac{4\pi N}{9k} \frac{\mu^2}{T} = 17.7 \pm 0.1 \text{ cc./g. mole}$$

and

$$\Gamma = 1.40 \pm 0.01$$

From the latter two we derive two physical constants of the material:

$$\mu = 0.50 \pm 0.02 \text{ Debye units}$$

and

$$\mu^2/TR = (0.65 \pm 0.015) \times 10^{-40}$$

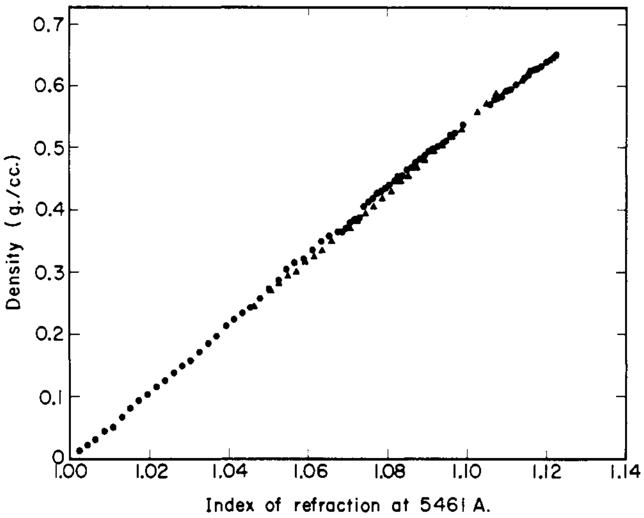

Figure 2. Density vs. index of refraction (circles indicates increasing density, triangles indicate decreasing density)

DISCUSSION

If it had been our purpose to achieve the highest accuracy in these measurements of R and μ, further experiments would have been done by using other compounds with known constants to check the procedures and equipment and by making additional runs with this compound to prove or improve the consistency of the observations. For our limited investigation, a lengthy systematic discussion of errors is not appropriate. The measurements were of 1%

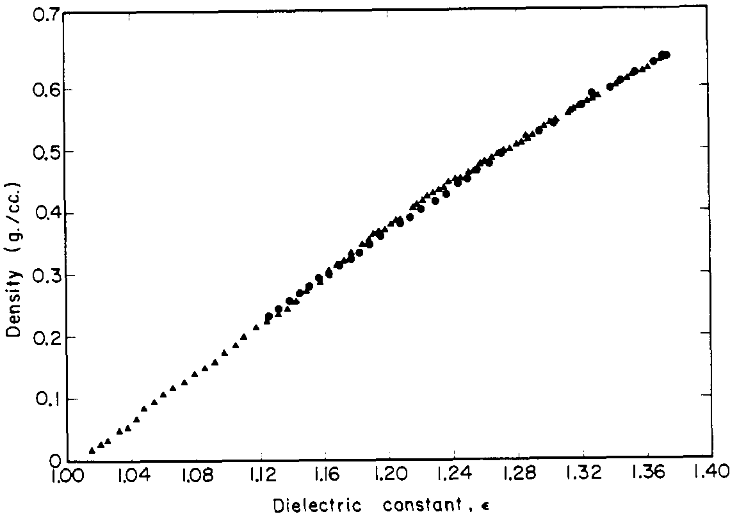

Figure 3. Density vs. dielectric constant (circles indicate increasing density, triangles indicates decreasing density)

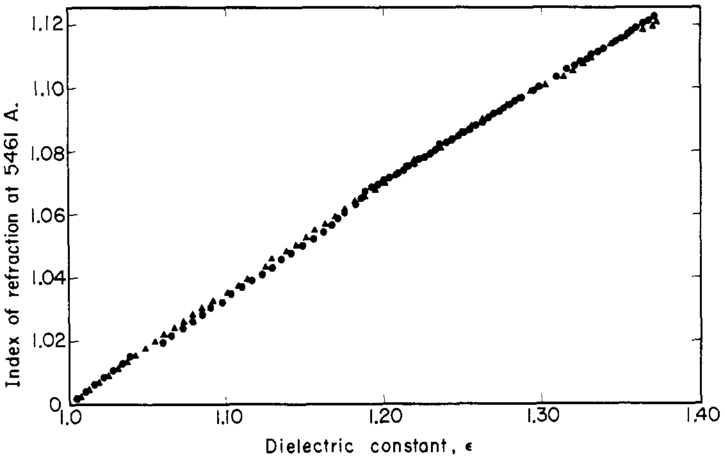

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Figure 4. Index of refraction vs. dielectric constant (circles indicate increasing density, triangles indicate decreasing density)

order of accuracy. Impurities in the compound were less than 1%. Other information in the literature does not seem entirely consistent, and our results are represented as useful, though perhaps not definitive.

To our knowledge, the molar refractivity has not previously been measured for this compound. On the other hand, the general subject has been well explored by physical chemists, and the constant, *R*, is predictable from the sum of the atomic refractivities of the constitutent atoms. Most of the values quoted in the literature are for the wave length 5890 A. (D line), and the tables of atomic refractivities are generally adjusted to be consistent with a large number of measurements on typical organic compounds. Several tables appear in the literature. The most frequently quoted one predicts a value of the molecular refractivity equal to 11.7. The atomic refractivity of fluorine appears to vary with the type of compound (*10*) and other subtleties. Von Grosse, who has worked with fluorine compounds, has estimated the molecular refractivity of Freon-13 to be approximately 12.08 for the D line (*7*) and not over 12.2 for 5461 A. (*6*).

Fuoss (*5*) measured the dielectric constant at 60 cycles and 29° C., and obtained a value of $R + (4\pi N/9k)(\mu^2/T) = 19.8$. He subtracts an estimated R of 15.17, thus giving a value for the dipole moment of 0.47 Debve units.

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