MEASUREMENT OF INDEX OF REFRACTION OF GASES AT HIGHER TEMPERATURES

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Abstract

The thermal coefficients of the indices of refraction of air, N_2, SO_2, NH_3, and CO_2.—For light of the visible spectrum these coefficients were not found to differ from the thermal coefficients of density change in the range 0–300°C. At 0°C, 760 mm the values of $(n-1)\,10^7$ for λ5852A, 6143A, and 6678A were found to be:

λ	Air	N_2	NH_3	CO_2	SO_2
5852A	2925	2985	3795	4485	6637
6143A	2919	2977	3785	4473	6615
6678A	2912	2969	3771	4465	6598

Incidentally the *rate of expansion of quartz with temperature* was found to be constant within the temperature interval 25–300°C, and to have an average value of expansion coefficient of $0.946(10)^{-6}$. A *kilowatt neon Geissler tube* is described.

A FABRY-PEROT interferometer was used to measure at higher than room temperatures the indices of refraction of several gases including some having polar molecules. It was hoped at the beginning of the experimental work that time would be had to extend the measurements into the infra-red. A recent article[1] gives very well the theory of the instrument and methods of use.

Apparatus. Fig. 1 will give an idea of the present experimental arrangement. It shows the optical system and an electric furnace encircling the Fabry-Perot interferometer. Light from a neon tube produced Haidinger interference fringes on the slit of the spectroscope. A camera photographed the fringes.
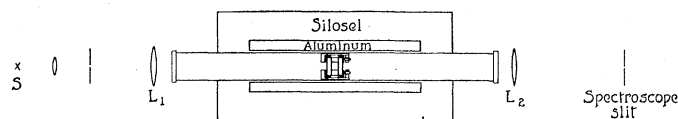

Fig. 1. Arrangement of apparatus.

The neon tube was constructed in the laboratory and furnished a particularly brilliant and satisfactory source for the interference work. The hard glass tube has large cylindrical electrodes, a narrow capillary about five inches long, and contains neon at a pressure of about 5 mm. The tube rests at two points in a water tank. (See Fig. 2.)

[1] W. H. J. Childs, J. Scientific Instruments **3**, Nos. 4 and 5 (1926).

Rubber tubing containing mercury makes the requisite flexible and water-tight seals around the lead-in wires. The tube has operated continuously for hours, with an input of a kilowatt furnished by a 10,000-v., 3-kw transformer.

The circular interferometer mirrors were made by sputtering platinum over their central portions in order to have inert surfaces. They remained good after heating in the furnace provided the glass had been baked for some hours before the sputtering. The laboratory mechanician ground on a lathe three fused quartz posts, (from the Hanovia Chemical Co.) for the etalon. For the more accurate adjustment of lengths, I ground the posts by hand on a flat steel disc. For testing the lengths of the posts one of the interferometer mirrors was mounted
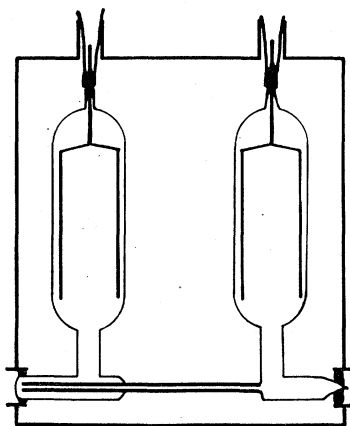

Fig. 2. The neon tube.

horizontally in a converging beam of mercury green light. The three quartz posts stood on this mirror. The second mirror, mounted in a light frame with levelling screws, rested on the quartz posts. By moving the top mirror a little with one or another of the levelling screws until the interference fringes appeared, it was easy to tell which quartz posts were longer. I ground the posts by hand until the Haidinger fringes showed the same order of interference over the whole of the mirrors when they were separated by the quartz posts. The mirrors and posts were then mounted in a steel cylinder about three inches long. Small coiled tungsten springs held the mirrors against the quartz posts. Steel springs were not satisfactory at higher temperatures, owing to variation in elasticity. The interferometer after adjustment was shoved to the center of a steel tube 35 inches long.

An electric furnace with a heating coil wound on a heavy cast aluminum cylinder to give uniform heat distribution surrounded 19 inches of the 35 inch steel tubing, which passed axially through the furnace. A can of Silosel insulated the furnace. This was mounted in a tank of water so that its heat capacity would reduce random temperature fluctuations. The water tank was mounted on screws so that the interferometer could be moved to bring the interference fringes accurately on the slit. Storage cells furnished the heating current and iron wire ballast lamps, kindly donated by the Edison Lamp Works of the General Electric Company, satisfactorily compensated for fall in voltage of the storage cells during long heating periods. With this arrangement the temperature in the furnace would remain constant to within 1/30 of a degree for hours. Changes in temperature of the interferometer due to the heat transference by the gases upon their entrance to the tube, however, caused trouble.

A copper-constantan thermocouple sealed in a glass tube projected through the casing of the interferometer until it was in the space between the interferometer plates. The thermocouple was heated for 50 hours at about 300°C, and then calibrated. A second calibration after 50 hours more of heating showed no change in the thermocouple. A potentiometer and a mirror galvanometer gave the electromotive force and could exhibit a change of 1/30°C in the temperature of the thermocouple. A Weston cell in a constant temperature bath served as a standard e.m.f.

Mercury in an inch bore manometer tube measured the gas pressure. Both surfaces of mercury could be raised and lowered simultaneously to prevent errors due to adhesion. A cathetometer which had been compared with a standard meter bar gave the heights of the mercury column and the readings were properly reduced to standard conditions.

A high grade photographic objective focussed the interference fringes upon the slit of the spectroscope. The rings were photographed on panchromatic plates and were measured with a traveling microscope reading to 1μ. The fractional order of interference at the center of the interference circles is equal to $Ad^2 - p$, where d is the diameter of the p'th ring from the center, and A is a constant for any one wave-length, i.e. $P/(d^2{}_{p-1} - d^2{}_p)$, where P is the order of interference. A is determined from measurements on two ring diameters and an approximate value of P. The A's are inversely proportional to the wave-lengths, so that A's measured for different lengths may be reduced to the A for some particular wave-length. This was done for measurements made on many lines and the values averaged, to give as good values for the

various constants as could be obtained with more effort from the usual formula involving the focal length of the projecting lens. The fractional order of interference at the center of the interference circles was determined to the third decimal place.

Preparation of gases. N_2 came from a commercial cylinder and passed over hot copper for elimination of oxygen. The air and N_2 filtered through six feet of drying tubes containing $CaCl_2$ and P_2O_5 and further passed through a liquid air trap on their way to the apparatus.
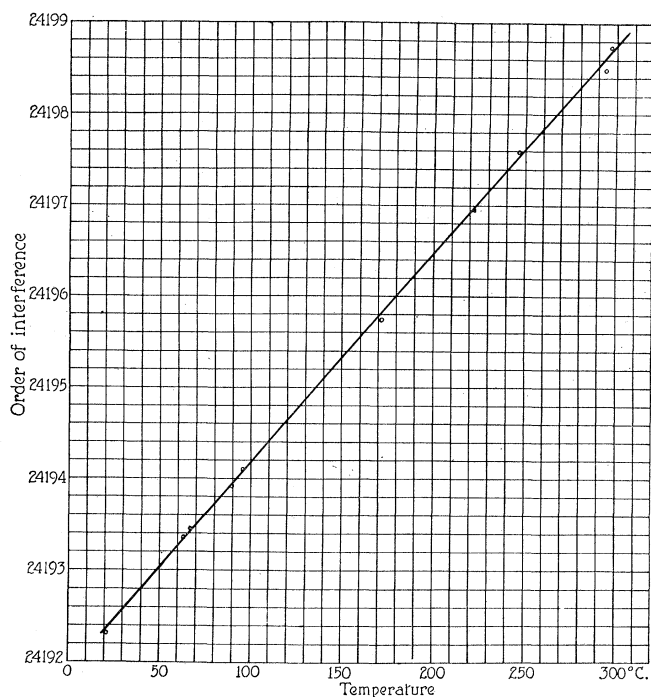

Fig. 3. The variation of the order of interference for vacuum with temperature.

HCl and marble in a Kipp generator furnished CO_2. This was dried by $CaCl_2$ and P_2O_5 and frozen in a liquid air trap. The middle portion of the sublimate was used each time.

The NH_3 came from a tank as a liquid. It boiled out of a Dewar flask equipped with an electric heating coil, and after passing over KOH, froze in the liquid air trap. The middle portion of the distillate was used.

The SO_2 came from a tank, was dried by passage through the drying tubes, and further purified by the usual freezing process.

Measurements. The index of refraction of a gas is given by dividing the order of interference with the gas between the plates by the order of interference with the interferometer evacuated. For the best results the pictures enabling these orders to be computed should be taken at precisely the same temperature. Unfortunately cooling by the admission of the gases made this procedure impossible. Although alterations in the interferometer with change in temperature were not quite continuous, the order of interference for the vacuum, at the same temperature as the gas under consideration, was obtained by interpolation from vacuum values at neighboring temperatures.

Fig. 3 shows the order of interference for a vacuum between the interferometer plates plotted against temperature. The order of interference at the lowest temperature plotted (21.4°C) is 24192.312.

TABLE I

Measured values of $(n-1) \times 10^6$ for various gases
Wave-length of light 5852A. Values reduced to 760 mm pressure

Temp. °K	$(n-1) \times 10^6$	Temp. °K	$(n-1) \times 10^6$
		Air	
294.5	270	445.1	180
338.3	236	508.1	153
363.1	221	567.5	148
		Nitrogen	
244.5	276	446.1	185
338.7	239	497.0	157
365.6	222	569.3	144
		Ammonia	
294.3	358	445.8	231
339.2	302	499.2	210
366.2	280	568.1	182
		Carbon dioxide	
294.4	411	439.4	277
333.7	373	483.6	247
363.5	334	567.6	222
		Sulfur dioxide	
294.3	612	434.4	418
335.1	537	481.2	371
360.1	499		

The expansion of the interferometer is shown to be moderately uniform. The slope of the line divided by the total order of interference, in Fig. 3, incidentally gives the average coefficient of expansion of quartz as 0.946×10^{-6} for the temperature interval 25°C–300°C, a figure higher than given in the tables. An attempt was made to account for the divergence of this value with Randall's measurements[2]

[2] Randall, Phys. Rev. **30**, 216 (1910).

on the thermal coefficient of expansion of quartz by taking account of change in length of the quartz posts due to change in tension of the tungsten springs. The required change in tension did not appear to be of a possible order of magnitude. Moreover, the rate of expansion of quartz with temperature is seen to be constant in the temperature interval 25°–300°C. This would seem to be in accord with expectation, but it disagrees with Randall's results. While the explanation of these discrepancies does not affect the discussion of the index of refraction of gases, it is still to be desired.

Table 1 summarizes the measurements on the indices of refraction at various temperatures. Measurements were made with pressures
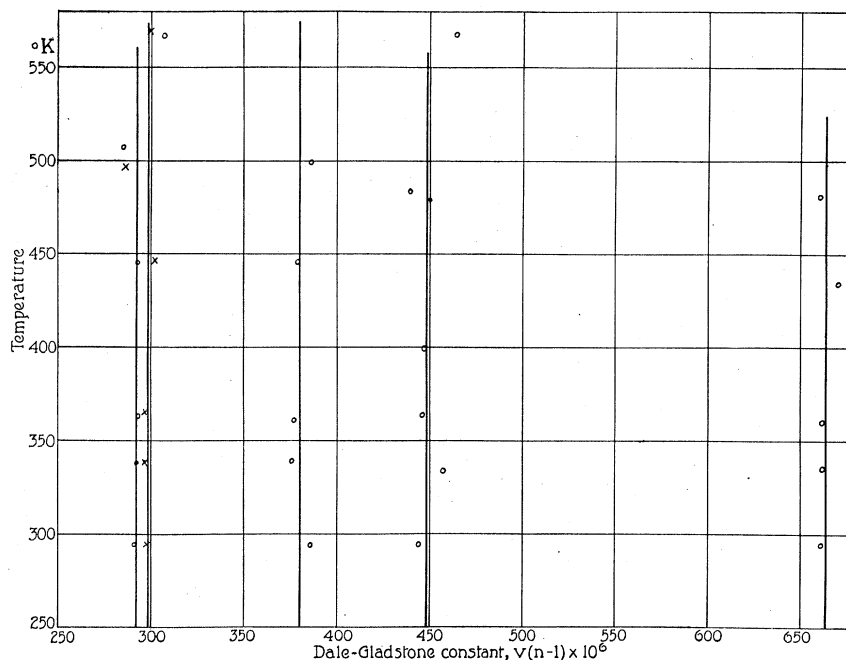

Fig. 4. The constant of the Dale-Gladstone law, $(n-1)v\times10^6$
plotted against temperature for the gases air, N_2, NH_3, CO_2, SO_2.

close to 760 mm and the readings reduced to values at 760 mm by multiplying by the inverse ratios of the pressures. Corrections for compression of the quartz by the gas are not necessary. Column 3 gives the indices of refraction of the wave-length 5852.488A reduced to standard pressure.

The Dale-Gladstone law states that $(n-1)v=$constant where v is the specific volume or is a number proportional to it. Fig. 4 shows $(n-1)v\times10^6$ plotted against temperatures for the various gases.

The volume v for the imperfect gases was computed by van der Waal's equation, taking v at 0°C to be 1 cc. No departure from the linearity required by the Dale-Gladstone formula can be detected from these measurements, or in other words, the thermal coefficient of the index of refraction is the same as the density coefficient. The measurements up to 150°C show less irrationality than do the measurements at higher temperatures. The lines are drawn giving equal weight to the four measurements at the lower temperatures. The intersections of these lines with the line $T = 273$°K give values of the indices of refraction of the various gases at 760 mm for 5852.488A in good agreement with the accepted values for the D line. Similar lines were drawn for the wave-lengths 6143.062A and 6678.276A. Table II gives the values of $(n-1) \times 10^7$ at 0°C, 760 mm for the various gases and various wave-lengths.

TABLE II

Values for $(n-1)$ 10^7 at 0°C, 760 mm pressure

Gas	λ5852A	λ6143A	λ6678A
Air	2925	2919	2912
N_2	2985	2977	2969
NH_3	3795	3785	3771
CO_2	4485	4473	4465
SO_2	6637	6615	6598

Theory[3] shows that in the infrared there may be a temperature coefficient of the index of refraction differing from the density coefficient for polar molecules, and measurements by Meggers and Peters[4] indicate such a temperature coefficient near the ultra-violet absorption bands in air. It should be interesting to study the temperature coefficient of the index of refraction in these regions.

I wish to express here my thanks to Dr. K. T. Compton for his encouragement and advice.

[3] P. Debye Phys. Zeit. **13,** 97 (1912).
[4] Meggers and Peters, Bulletin of the Bureau of Standards **14,** 371 (1917).