

was made wider and a series of exposures at different times made on the same plate. Microphotometer traces of these were run on the same paper with traces of corresponding interferometer patterns, but the plate calibrations in the case of silver were only used in selecting the peaks of the traces to be analyzed. The greater lack of resolution in the microphotometer traces of the silver lines made the analysis of the peaks more difficult than the example shown by Granath and Van Atta for sodium. The resolution of the silver resonance lines obtained to date does not justify making such corrections as are mentioned by Tolansky and Heard<sup>11</sup> in their work on the fine structure multiplet of As II. The intensity calibrations and the microphotometer traces showed that possibly the fourth to eighth fringes inclusive might give approximately the intensity ratio of the two components of  $\lambda 3383$ .

<sup>11</sup> S. Tolansky and I. F. Heard, Proc. Roy. Soc. **A146**, 818 (1934).

Traces of  $\lambda 3281$ , taken from exposures of very low intensity due to the very low currents that had to be used, showed too much variation and hence were not measured. Traces from seven plates of  $\lambda 3383$  were measured giving the following averages: 1.87, 1.54, 1.80, 1.85, 1.64, 1.76, 1.72; with a general average of 1.74. This average lies between 3, the theoretical value for the intensity ratio when  $I$  is  $\frac{1}{2}$  (if it is supposed that the spectral line has only two components, in this case originating from the  $^2S$  lower level), and 1.67 the theoretical value when  $I$  is  $3/2$ . If the structure is due to a spin, and half integral values only are to be considered because the mass numbers of both isotopes are odd, then 1.74 suggests that the nuclear spin of silver is  $3/2$ .

The writer wishes to acknowledge the interest and assistance of Professor George S. Monk who suggested the problem, and under whose direction the work was done. It is also a pleasure to thank Professor Carl Eckart and Professor R. S. Mulliken for helpful advice.

## The Electro-Optical Kerr Effect in Ammonia, Nitrogen and Oxygen

WILLIAM M. BREAZEALE, *University of Virginia*

(Received June 7, 1935)

Absolute values for the Kerr constant in anhydrous ammonia, nitrogen and oxygen have been determined. Measurements in  $\text{NH}_3$  were made at wavelengths of 6500A and 5750A, pressures from 13 to 30 atmospheres, and temperatures from 40° to 80°C. In  $\text{N}_2$  and  $\text{O}_2$  the wavelength used was 6500A, pressures in the neighborhood of 100 atmospheres and temperatures from 20° to 65°C. The absolute value for the Kerr constant reduced to N. P. T. and 6500A is for  $\text{NH}_3$   $(62.3 \pm 1.8)10^{-12}$ , for  $\text{N}_2$   $(4.64 \pm 0.10)10^{-12}$  and  $\text{O}_2$   $(6.94 \pm 0.30)10^{-12}$ .

### INTRODUCTION

WHEN certain isotropic substances are placed in an electric field they acquire the optical properties of a uniaxial crystal with the optic axis in the direction of the electric field. The law governing this phenomenon, first determined by Kerr, states that the phase difference  $D$ , in radians, between the two components of the light beam is given by

$$D = 2\pi l(n_p - n_s)/\lambda = 2\pi B l E^2, \quad (1)$$

where  $n_p$  and  $n_s$  are the refractive indices corresponding to electric vectors parallel and perpendicular to the electric field, respectively,  $l$  the length of the light path through the electric field,  $\lambda$  the wavelength,  $E$  the field strength in e.s.u., and  $B$  the so-called Kerr constant.

If plane polarized light is passed through the field, the electric vector making an angle of 45° with the direction of the field, the relation between the intensities of the components is given by

$$D = 2 \arcsin (I_k/I_0)^{\frac{1}{2}}. \quad (2)$$

Here  $I_0$  is the total intensity of the light passing through the Kerr cell and  $I_k$  the intensity of the Kerr beam which, when the polarizer and analyzer are parallel, will appear only when the electric field is applied.

A combination of (1) and (2) gives

$$B = (1/\pi l E^2)(I_k/I_0)^{\frac{1}{2}}. \quad (3)$$

This is the equation used to determine  $B$  from the quantities measured in this experiment. Here the argument is set equal to the arc sine, but since  $D$  is small in these experiments, the error introduced is negligible.

From the Langevin-Born theory of the Kerr effect<sup>1, 2</sup> the Kerr constant  $B$  for a nonpolar gas such as oxygen or nitrogen is given by

$$B = [(n^2 - 1)(n^2 + 2)(\epsilon + 2)^2/n\lambda] \cdot C_1/T \quad (4)$$

and for a polar gas such as ammonia,

$$B = [(n^2 - 1)(n^2 + 2)(\epsilon + 2)^2/n\lambda] \times (C_1/T + C_2/T^2). \quad (5)$$

Here  $n$  is the index of refraction,  $\epsilon$  the dielectric

constant,  $\lambda$  the wavelength, and  $C_1$  and  $C_2$  constants independent of density, temperature and wavelength. These equations have been tested experimentally and found to hold for gases; they are used to reduce the value of  $B$  measured at any particular density, temperature and wavelength to that at N. P. T. and the desired wavelength. Quantum-mechanical treatment by Serber<sup>3</sup> merely adds a correction term which becomes appreciable only in the ultraviolet.

Ammonia and nitrogen were measured directly but fire hazard prevented doing this with oxygen. Instead the Kerr constant of a mixture of nitrogen and oxygen was measured and the Kerr constant for oxygen determined from this and the known value for nitrogen. The relation used in determining the value for oxygen is obtained as follows. For constant temperature and wavelength Eq. (4) reduces to

$$B = (n^2 - 1)(n^2 + 2)(\epsilon + 2)^2 C/n, \quad (6)$$

where  $C$  is another constant. Now  $(\epsilon - 1)$  and  $(n^2 - 1)$  and, to a sufficient degree of accuracy for our purposes,  $(n - 1)$  are additive in a mixture of nitrogen and oxygen. Hence for the mixture

$$B_m = \frac{[(n_1^2 - 1) + (n_2^2 - 1)][n_1^2 + n_2^2 + 1][\epsilon_1 + \epsilon_2 + 1]^2}{n_1 + n_2 - 1} \cdot C_m. \quad (7)$$

Here the subscripts 1, 2 and  $m$  distinguish the properties of the first and second gases and the mixture. (7) can be rewritten

$$B_m = (n_1^2 - 1) \frac{(n_1^2 + n_2^2 + 1)(\epsilon_1 + \epsilon_2 + 1)^2}{n_1 + n_2 - 1} C_m + (n_2^2 - 1) \frac{(n_1^2 + n_2^2 + 1)(\epsilon_1 + \epsilon_2 + 1)^2}{n_1 + n_2 - 1} C_m. \quad (8)$$

Setting the first half of the right-hand member equal to a new constant  $B_1'$  and dividing by the value for  $B_1$  given by (6) gives

$$B_1' = B_1 \frac{n_1(n_1 + n_2 + 1)(\epsilon_1 + \epsilon_2 + 1)^2 C_m}{(n_1 + n_2 - 1)(n_1^2 + 2)(\epsilon_1 + 2)^2 C_1}. \quad (9)$$

<sup>1</sup> Langevin, *Le radium* 7, 249 (1910); Born, *Ann. d. Physik* 55, 177 (1918).

<sup>2</sup> For a résumé of the derivation of this theory see Beams, *Rev. Mod. Phys.* 4, 133 (1932), or Stuart, *Molekulstruktur* (Julius Springer, 1934).

A similar expression can be written for  $B_2'$ . Substituting in (8) gives

$$B_m = B_1' + B_2'. \quad (10)$$

The value for  $C$  obtained from the theory of the Kerr effect<sup>2</sup> is

$$C = \frac{(\epsilon - 1)(n - 1)}{36\pi N k T \lambda (n^2 - 1)} \cdot \frac{\Delta}{6 - 7\Delta}. \quad (11)$$

Here  $N$  is the number of molecules per cc,  $k$  is Boltzmann's constant,  $\Delta$  is the light scattering coefficient and  $\epsilon$  and  $n$  are values of the dielectric constant and refractive index at N. P. T. However, all that is necessary for calculation is the ratio of  $C_1$  to  $C_2$ . This is given by

$$\frac{C_1}{C_2} = \frac{\Delta_1(\epsilon_1 - 1)(n_1 - 1)(n_2^2 - 1)(6 - 7\Delta_2)}{\Delta_2(\epsilon_2 - 1)(n_2 - 1)(n_1^2 - 1)(6 - 7\Delta_1)}. \quad (12)$$

<sup>3</sup> Serber, *Phys. Rev.* 43, 1011 (1933).

TABLE I. *Kerr constant in ammonia.*

1	2	3	4	5	6
PRESSURE (ATMOS.)	TEMP. (°C)	WAVE- LENGTH (Å)	FIELD (E.S.U.)	$B$ STD. DEN. ( $\times 10^{12}$ )	N.P.T. AND 6500Å ( $\times 10^{12}$ )
13.7	40.8	5750	75.5	54.0	63.2
13.6	41.1	5750	76.9	53.4	62.5
22.0	59.8	5750	76.4	46.5	61.2
21.8	61.1	5750	82.1	46.5	61.6
32.2	81.0	5750	79.7	41.0	61.0
30.6	79.7	5750	89.8	43.8	64.7
13.5	41.4	6500	72.3	48.4	64.1
13.7	39.7	6500	75.1	46.8	61.4
14.3	60.5	6500	72.4	42.0	62.6
22.2	60.7	6500	83.0	42.0	62.8
15.1	78.1	6500	72.4	38.1	63.0
31.1	81.8	6500	94.5	36.9	62.4
				Mean	62.6

Since  $C$  is a function of the molecular structure, it is safe to assume that

$$C_m = f_1 C_1 + f_2 C_2, \quad (13)$$

where  $f_1$  and  $f_2$  are the fractional number of molecules of the first and second gases in the mixture. This, then, provides a means of calculating the ratios  $C_m/C_1$  and  $C_m/C_2$ .

Since  $B_m$  is measured and  $B_1$  is known,  $B_1'$  can be calculated from (9) and (12). Eq. (10) then gives  $B_2'$  and by using an equation similar to (9)  $B_2$  can be deduced.

#### EXPERIMENTAL METHOD

The experiments were performed using a method developed by Stevenson and Beams<sup>4</sup> and improved by Bruce<sup>5</sup> and Quarles.<sup>6</sup> The principal advantage of this method is that it permits the use of high gas pressures and higher

TABLE II. *Kerr constant in nitrogen.* Wavelength = 6500Å.

1	2	3	4	5
PRESSURE (ATMOS.)	TEMP. (°C)	FIELD (E.S.U.)	$B$ STD. DEN. ( $\times 10^{12}$ )	N.P.T. AND 6500Å ( $\times 10^{12}$ )
106.6	20.1	360	4.22	4.53
101.5	20.0	357	4.27	4.58
108.1	45.0	344	3.95	4.60
110.7	65.1	358	3.90	4.83
			Mean	4.64

<sup>4</sup> Stevenson and Beams, Phys. Rev. **38**, 133 (1931).

<sup>5</sup> Bruce, Phys. Rev. **44**, 689 (1933).

<sup>6</sup> Quarles, Phys. Rev. **46**, 692 (1934).

electric fields with a consequent increase in the magnitude of the effect.

The apparatus used was essentially the same as that described by Bruce and Quarles. The only major change was the substitution of a more sensitive amplifier.

The anhydrous ammonia was obtained by evaporation from a commercial tank of the liquid. Conductivity tests of the liquid indicated that it contained less than 0.01 percent water. The nitrogen and oxygen were taken from commercial cylinders of these gases. The manufacturers' analysis gave about 0.5 percent impurities, mainly rare gases. A correction was made to the pressure for these. In all cases the Kerr cell was evacuated and dried before the gases to be measured were admitted.

#### RESULTS

The results of the measurements of the Kerr constant  $B$  in anhydrous ammonia are shown in Table I. The first four columns give the experimental conditions under which the measurements were made. The fifth column gives the Kerr constant at standard density but at the temperature and wavelength of measurement computed with the aid of Eq. (5). This column then shows the variation of  $B$  with temperature for two wavelengths. The sixth column gives  $B$  reduced to its value at N. P. T. and 6500Å again by the use of Eq. (5). The constancy of this column is a measure of the precision of the measurements and the reduction formulae. The variation of  $B$  with temperature is shown graphically in Fig. 1. The experimental points are shown by circles while the solid line is the theoretical curve plotted from Eq. (5).

TABLE III. *Kerr constant in oxygen.* Wavelength = 6500Å.

1	2	3	4	5	6
PRESSURE NITROGEN (ATMOS.)	PRESSURE MIXTURE (ATMOS.)	TEMP. (°C)	FIELD (E.S.U.)	$B$ STD. DEN. ( $\times 10^{12}$ )	N.P.T. AND 6500Å ( $\times 10^{12}$ )
43.1	106.5	20.1	334	6.52	7.00
45.3	108.1	20.1	335	6.38	6.83
67.3	109.7	20.1	333	6.21	6.67
66.8	110.3	20.1	335	6.47	6.94
51.3	107.1	44.9	334	6.10	7.10
52.8	111.3	65.0	334	5.75	7.12
				Mean	6.94

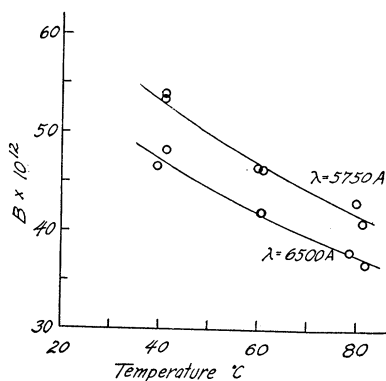


FIG. 1. Temperature variation Kerr effect in ammonia.

Table II shows the results of the measurements in nitrogen. The fourth and fifth columns were determined with the aid of Eq. (4). Since it has been well established that gases obey the Langevin-Born theory, effort was concentrated on determining absolute values of the Kerr constant rather than its variation with density, temperature, etc. To this end measurements were made under only a few different conditions, but a large number of readings were taken at each point.

The value for the Kerr constant of oxygen as determined from measurements in the nitrogen-oxygen mixtures is shown in Table III.  $B$  for oxygen was determined as previously described and the results reduced to N. P. T. using Eq. (4). The density of the individual gases in the mixture was computed with the aid of the Beattie-Bridgman equation of state using a linear combination of constants as described by Beattie and Ikehara.<sup>7</sup>

Values of the index of refraction for these calculations were determined with the aid of the Lorentz-Lorenz relation which, Occhialini<sup>8</sup> has shown, holds with sufficient accuracy for these experiments. Zahn<sup>9</sup> has measured the variation of  $(\epsilon-1)$  with temperature and density for ammonia and shows that it follows Debye's equation,  $(\epsilon-1) \nu T = AT + B$ . Debye's equation with Zahn's experimental values for  $A$  and  $B$

<sup>7</sup> Beattie and Ikehara, M. I. T. publications, Serial No. 239.

<sup>8</sup> Occhialini, Nuovo cimento (6) 8, 123 (1914).

<sup>9</sup> Zahn, Phys. Rev. 27, 455 (1926).

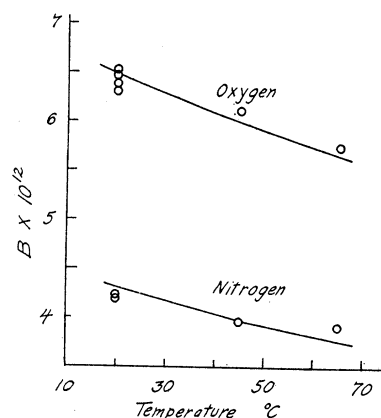


FIG. 2. Temperature variation Kerr effect in nitrogen and oxygen.

was used to calculate  $\epsilon$  for ammonia at the various points.

Fig. 2 shows graphically the variation of  $B$  with temperature for nitrogen and oxygen. Again the circles are experimental points and the solid lines theoretical curves calculated this time from Eq. (4).

The absolute value of the Kerr constant for these three gases at N. P. T. and 6500A is for ammonia  $(62.6 \pm 1.8)10^{-12}$ , for nitrogen  $(4.64 \pm 0.10)10^{-12}$ , and for oxygen  $(6.94 \pm 0.30)10^{-12}$ . Szivessy<sup>10</sup> gives  $59 \times 10^{-12}$  for  $B$  in ammonia at one atmosphere, 17.5°C and 5890A. Reduced to N. P. T. and 6500A this would be  $64 \times 10^{-12}$ . Bruce,<sup>5</sup> from an indirect comparison with carbon dioxide, obtained  $5.7 \times 10^{-12}$  for  $B$  in nitrogen at one atmosphere, 34.6°C and 4550A. This corresponds to  $5.1 \times 10^{-12}$  at N. P. T. and 6500A. The author knows of no experimental value for  $B$  in oxygen. The theoretical value calculated on the basis of the Langevin-Born theory is  $6.49 \times 10^{-12}$  at N. P. T. and 6500A.

#### ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. J. W. Beams under whose direction this work was done, to Dr. L. G. Hoxton for assistance in preparation of the manuscript, and to Dr. W. E. Deming of the Fixed Nitrogen Laboratory for valuable suggestions in computing densities of mixtures.

<sup>10</sup> Szivessy, Zeits. f. Physik 26, 323 (1924).