ELECTRIC AND MAGNETIC DOUBLE REFRACTION

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A. INTRODUCTION

THE branches of physics known as electro-optics and magneto-optics originated in 1845 with the discovery by Michael Faraday that plane polarized light has its plane of polarization rotated when traversing a transparent medium parallel to the lines of force of a magnetic field. This epoch making discovery of Faraday's was the result of his long search for a relation between light, electricity and magnetism. For, as he says in his paper announcing the discovery,[1] "I have long held an opinion, almost amounting to a conviction, in common I believe with many other lovers of natural knowledge, that the various forms under which the forces of matter are made manifest have one common origin; or, in other words, are so directly related and mutually dependent, that they are convertible, as it were, one into the other, and possess equivalents of power in their action". This conviction of Faraday's led him to search further for other relations between light, electricity, and magnetism, but the sensitivity of his apparatus was not sufficient to reveal the many connections that have since been established. It can justly be said, moreover, that the early ideas and work of Faraday have been a constant inspiration and urge to others to apply improved technique to the further search for new phenomena in the field of electro- and magneto-optics. Illustrations of this influence are numerous in the literature but perhaps the most notable examples are to be found in the important discoveries of Kerr, Zeeman, and Cotton and Mouton of the effects which bear their respective names. In fact, with the possible exception of the photoelectric effect, most of the primary discoveries in electro- and magneto-optics resulted from a deliberate attempt on the part of the experimenter to improve his apparatus until a relation could be observed. It is obvious, therefore, that considerable difficulty would be encountered in attempting completely to discuss some of the connections between light, electricity and magnetism without including

[1] Experimental Researches, Vol. III, p. 1.

most of the others. However, to do this at the present time would lead into too lengthy a discussion and perhaps into unnecessary repetition. In this article an attempt will be made to give a resumé of what seems the most important work done up to the present time on the effects produced on light when traversing a substance in a direction perpendicular to the lines of force of a magnetic or an electric field. The principal part of the discussion will be confined to the two effects usually called the Kerr electro-optical effect and the Cotton-Mouton effect after their respective discoverers. In every case an effort will be made to give such references to the literature as will make it possible for those who are especially interested to study further.

B. ELECTRIC DOUBLE REFRACTION

(1) The Kerr electro-optical effect

Kerr,[2] in 1875, was the first to succeed in observing that, when an electric field is established in some isotropic substances they become doubly refract-
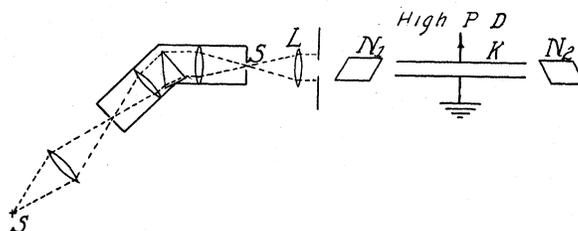
Fig. 1.

ing (or birefringent) with their "optic axes" parallel to the lines of force, or that the substance, when placed in a uniform electrostatic field, assumes the properties of a uniaxial crystal with its optic axis parallel to the lines of electric force. The effect can best be shown by an arrangement similar to that in Fig. 1.

Monochromatic light is made parallel by a lens L, plane polarized by a nicol prism N_1, passes between two parallel metallic plates called a "Kerr cell" K and to a second nicol prism N_2 "crossed" with respect to N_1. For the maximum effect the plane of transmission of N_1 is made 45° with the lines of force. If the two metallic plates of K are at the same electric potential no light will pass N_2, since the substance under investigation in K is isotropic. However, when an electrostatic field is applied across the plates of K, the substance becomes doubly refracting, i.e. the component of the light vibration parallel to the lines of force traverses the medium with a different velocity from the vibration perpendicular thereto. The light, therefore, emerges from K elliptically polarized and a part of it can pass N_2. The sign of the ellipticity of the emergent light remains unchanged if the direction of the electric field in K is reversed. Also, the magnitude of the effect is doubled if

[2] Kerr, Phil. Mag. [4], 50, 337 (1875).

the light is reflected back on its path through K by a mirror placed between K and N_2.

The first substance used by Kerr was a block of glass in which the terminals of an induction coil were embedded. With the electric field on, the glass behaved optically as if it had been placed under mechanical tension in a direction parallel to the lines of force, i.e., like a positive crystal, say quartz. In some other solids, such as resin colophonium, the effect was opposite to that of glass, i.e., they behaved optically like glass compressed in the direction of the lines of force or like a crystal of Iceland spar. The phenomenon did not appear simultaneously with the application of the electric field but sometimes required several seconds to reach full value (half a minute in the case of glass). A similar time existed between the removal of the field and the vanishing of the double refraction. This slowness with which the effect appeared and disappeared led to considerable speculation as to the true origin of the phenomenon. It seemed likely that it resulted from strains in the substance set up by the electric field, for from the work of Volta it was well known,[3] for example, that "the dielectric in a glass condenser when charged expanded and became the seat of electric strain". Another hypothesis put forward was that the effect was due to an increase of temperature resulting from electrical conduction in the substance. Kerr, however, did not believe that the effect which he had discovered was purely of mechanical or thermal origin. He initiated, therefore, a search for the effect in isotropic nonviscous liquids where strains of appreciable magnitudes could not be induced by the field. He immediately found the phenomenon in a large number of liquids.[4] In some, such as carbon disulphide, paraffin oil, toluene, and benzene the double refraction was positive while in others, such as olive oil, colza oil, and seal oil it was negative. In every case, as far as he could determine, the effect appeared and disappeared simultaneously with the application and removal of the electric field, which was good evidence that the phenomenon was of electrical origin. This discovery of the effect in both solids and liquids immediately aroused the interest of many workers, with the result that the experiments of Kerr were promptly confirmed and extended.[5-10]

In his early work Kerr[4,11] was able to establish the relationship between the magnitude of the double refraction and that of the electric field strength. Briefly the law states that, if n_p and n_s are the refractive indices for the components of the light vibration parallel and perpendicular to the lines of force

[3] See Govi, C. R. **87**, 857 (1878); Duter, C. R. **87**, 828 (1878); **88**, 1260 (1879); Righi, C. R. **88**, 1260 (1879); Quincke, Wied. Ann. **10**, 161 (1881); **10**, 513 (1881); **19**, 545 (1883); Pauthenier, Jour. de Physique **5**, 312 (1924).

[4] Kerr, Phil. Mag. [4], **50**, 446 (1875); [5], **8**, 85 (1879); [5], **8**, 229 (1879).

[5] Gordon, Phil. Mag. [5], **1**, 203 (1876); Proc. Roy. Soc. **A28**, 346 (1879).

[6] Mackenzie, Wied. Ann. **7**, 356 (1877).

[7] Guthrie, Nature **16**, 264 1876).

[8] Quincke, Wied. Ann. **10**, 536 (1880).

[9] Röntgen, Wied. Ann. **10**, 77 (1880).

[10] Brongersma, Wied. Ann. **16**, 222 (1882); Phil. Mag. [5], **14**, 127 (1883).

[11] Kerr, Phil. Mag. [5], **9**, 157 (1880); [5], **13**, 153, 248 (1882).

in the substance, respectively, their phase difference D in radians after passing through an electric field E expressed in e.s.u. is

$$D \equiv \frac{2\pi l(n_p - n_s)}{\lambda} = 2\pi BlE^2 \tag{1}$$

where λ is the wave-length of the light, l is the length of the light path in cm through the electric field in the substance, and B is called the Kerr constant. The latter, however, has been found to vary with different substances, wave-lengths, and temperatures. This law of Kerr's has been found to hold with accuracy by almost all of the workers in the field since it was proposed. The few exceptions[12] have been expained as errors in the method of measurement, for careful repetition by subsequent workers[13,14] have failed to find the deviations reported. In carbon disulphide Chaumont[15] found the exponent of E to be 2.0045, and concluded that as far as he was able to observe Kerr's law was exact for clean carbon disulphide. This conclusion has recently been substantiated[16] for the nonpolar, nonconducting carbon disulphide, but in the case of some polar liquids a very slight deviation was indicated at high field strengths. Deviations from Kerr's law at high field strengths have also been noted in crystals.[17]

(2) Experimental methods of measuring the Kerr constant B

To determine the value of B for a given temperature, wave-length, and substance, it is clear from Eq. (1) that it is necessary to measure E, l, and D. For example, if Eq. (1) is rewritten in terms of the quantities experimentally measured in the case of a Kerr cell with plane parallel plates spaced a distance a,

$$D = 2\pi Bl \frac{V^2}{a^2} \tag{2}$$

where V is the potential applied across the cell. Hence various experimental methods have been a sequence of improvements in the technique of measuring the electrical potential across the cell, the dimensions of the cell (especially the distance between its plates and the end corrections), and the ellipticity of the emergent light. In general the arrangements fall into two principal classes depending upon whether or not the substance is electrically conducting or nonconducting. If nonconducting, a modified form of Kerr's method is usually used but if conducting, a method first used by Des Coudres[18] is employed by which the Kerr constant of the substance is determined in terms of that of a substance with a known Kerr constant.

[12] Elmen, Phys. Rev. **20**, 54 (1905); Ann. d. Physik **16**, 350 (1905).

[13] Morse, Phys. Rev. **23**, 252 (1906).

[14] McComb, Phys. Rev. **27**, 336 (1908); **29**, 525 (1909).

[15] Chaumont, Ann. de Physique **5**, 64 (1916).

[16] Beams, Phys. Rev. **37**, 781 (1931).

[17] Müller, Bulletin Am. Phys. Soc. **6**, 11 (1931).

[18] Des Coudres, Verh. d. Ges. deutsch. Naturf. u Ärtz **65**, vers Nürnberg **2**, 67 (1893).

In the first method the light is usually made monochromatic by filters or a monochromatic illuminator and in the best work the Kerr cell is thermostatically controlled. The end windows of the Kerr cell should be free from strain, so that with the electric field removed, there is no residual double refraction. The metallic plates of the Kerr cell are usually plane and rigidly mounted parallel in insulating supports. It is important that these plates be large enough to give a uniform electric field over the region traversed by the light. To insure this the plates are usually spaced but a few millimeters apart, so that it is necessary to measure this distance a with high precision since it is squared in Eq. (2). The effective length of the plates or of the electric field also presents difficulties because of the end corrections that must be applied. The problem of determining the distortion of the field at the end of the condenser has been solved by numerous investigators.[19–22] Also it is often possible approximately to determine the end corrections experimentally by using cells of different lengths.[14] The potentials V across the Kerr cell have usually been supplied by a static machine, transformer and rectifier or storage battery and the magnitude of the potential measured by an electrostatic voltmeter, potentiometer or ordinary voltmeter. It is clear from Eq. (2) that an error of one percent in V will produce an error of two percent in B. In most substances B is comparatively small so that it is necessary to have a large value of V to make D of conveniently measurable size. Unfortunately the technique of measuring as well as producing high steady potentials has not been developed to a satisfactory stage for measuring Kerr constants so that the precision of B is usually limited by that of V. In fact, the process has often been reversed and the Kerr cell used as a high potential voltmeter.[23] The value of D which is a measure of the double refraction has been determined in a variety of ways. In general, however, there are two principal methods, one of which depends upon the measurement of the displacement of a dark band (Babinet compensator),[24] and the other upon the matching of the different parts of a field of view. The latter methods are by far the more accurate and have been used almost exclusively since the work of Brace[25] on his ingenious half shade arrangement, with which a precision of one twenty thousandth of a wave-length has been claimed. Several excellent treatments of the various methods of measuring the magnitude of double refraction exist,[26–30] as well as their application to the measurement of D.[13,14,15,28,29] Therefore it is not

[19] Maxwell, Electricity and Magnetism Vol. 1. 3rd Ed. Clarendon Press, 1892.

[20] Lemoine, C. R. 122, 835 (1896).

[21] Chaumont, Ann. de Physique 5, 17 (1916).

[22] Szivessy, Handbuch der Physik 21, 733 (1929).

[23] Pungs and Vogler, Phys. Zeits. 31, 485 (1930).

[24] Wood, Phys. Optics 333, (1923); Houstoun, Treatise on Light, 224, 413 (1919).

[25] Brace, Phys. Rev. 18, 70 (1904); 19, 218 (1904).

[26] Skinner, J.O.S.A. and R.S.I. 10, 491–520 (1925).

[27] Chaumont, Ann. de physique 4, 101–206 (1915).

[28] Szivessy and Münster, Zeits. f. Physik 53, 13 (1929); See Szivessy, Handbuch der Physik 19, 917–972, Julius Springer (1928).

[29] Hagenow, Phys. Rev. 27, 196 (1908).

[30] Szivessy, Zeits. f. Krist. 77, 239 (1931).

necessary to discuss these methods further. Recently[31] good precision has been attained by applying the photoelectric cell to the measurement of D.

When the substance is conducting, the above method cannot be used because of the impossibility of maintaining a steady electric field across the Kerr cell without the medium heating or decomposing. Hence it is necessary to apply the potential to the cell suddenly and quickly remove it before sufficient conduction can take place appreciably to change the temperature. The general scheme used by Des Coudres, Schmidt,[32] and others[33] is illustrated by Fig. 2.

Monochromatic light is plane polarized by a nicol prism N_1 oriented so that its plane of transmission makes 45° with the vertical, passes into a Kerr cell K_1 with its plates vertical, then into a second Kerr cell K_2 with its plates horizontal, and finally into the nicol N_2 crossed with respect to N_1. If now a substance with a known Kerr constant B_1 is placed in K_1, it is possible to determine the unknown Kerr constant B_2 of a substance placed in K_2 (provided B_1 and B_2 are of the same sign. If B_1 and B_2 are of opposite signs the plane of the plates of K_2 are made parallel to that of K_1). The procedure often con-
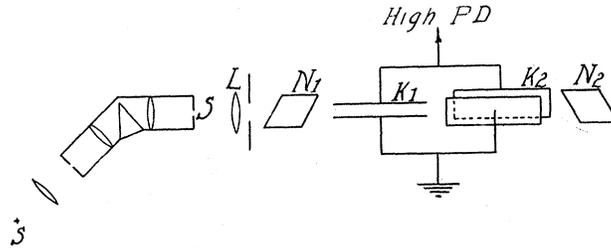
Fig. 2.

sists in applying the same potential across the two cells, making the distance between the plates of K_2 variable and adjusting until the double refraction in K_1 is compensated by that in K_2 i.e., until no light passes N_2 then

$$\frac{B_1}{B_2} = \frac{a_1{}^2 l_2}{a_2{}^2 l_1}.$$ (3)

(It might be noted that it is important to have the planes of the plates of the two cells accurately perpendicular (or parallel) to avoid a rotation of the plane of polarization.)

(3) Theory of the Kerr electro-optical effect

Although the classical theories of Drude[34] and Voigt[35] and others[36] were remarkably successful in explaining the phenomena of ordinary dispersion,

[31] Stevenson and Beams, Phys. Rev. **38**, 133 (1931).
[32] Schmidt, Ann. d. Physik **7**, 142 (1902).
[33] Lyon, Ann. d. Physik **46**, 753 (1915).
[34] Drude, Theory of Optics, 358–456, Longmans, 1902.
[35] Voigt, Magneto and Elektrooptik, Leipzig, 1908. Ann. d. Physik **4**, 197 (1901).
[36] Lorentz, Theory of Electrons, 132–167, Leipzig, 1909.

absorption, and even the Faraday effect, they were notably unsuccessful when directly applied to that of electric and magnetic double refraction, or more specifically, the electro-optical Kerr effect and the Cotton-Mouton effect. It was soon surmised that this discrepancy in both the two above effects between theory and experiment perhaps had its origin in the anisotropy of the magnetic, electrical and optical properties of the molecules of an isotropic medium. Confining ourselves first to a consideration of the Kerr electro-optical effect* we find that Havelock[37] was among the first to formulate an hypothesis that brought a large number of the experimental results into accord. He imagined "an effective cavity to be associated with each particle such that the force on the particle is the force within such a cavity in a medium uniformly polarized to the value of the material polarization vector at the point in question". For an isotropic medium the "cavity" was taken to be a sphere but with the application of the electric field changed into an ellipsoid. Physically, he preferred to visualize this change as brought about by a different spacing of similar molecules along and perpendicular to the field, although he points out that it might possibly be due to an orientation of similar anisotropic molecules by the field. With these assumptions he shows that

$$n_p = n - \frac{2}{15} \frac{(n^2 - 1)^2}{n} \epsilon$$

$$n_s = n + \frac{1}{15} \frac{(n^2 - 1)^2}{n} \epsilon \qquad (4)$$

where n_p and n_s are the indices of refraction parallel and perpendicular to the electric field, n is the index of refraction with the field removed, and ϵ is a constant independent of the wave-length. Hence from Eq. (1),

$$B = \frac{c}{E^2} \frac{(n^2 - 1)^2}{\lambda n} \qquad (5)$$

where c is a constant and independent of λ, the wave-length of the light, also

$$\frac{(n_p - n)}{(n_s - n)} = -2. \qquad (6)$$

Eq. (5) connects the dispersion of the electric double refraction with the ordinary dispersion of the isotropic medium. It is known as Havelock's law and has been verified experimentally over the visible range by many different investigators.[14,29,38] Eq. (6) has also been verified especially by Ackerlein[39] Pauthenier[40] and Larkin.[41]

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* The same type of theories can be used to explain both the Cotton-Mouton effect and the Kerr electro-optical phenomenon. In fact in most cases the formulas derived for the latter can be utilized for the former merely by substituting the analogous magnetic constants for the electrical constants.

[37] Havelock, Proc. Roy. Soc., A80, 28 (1907); A84, 492 (1911); Phys. Rev. 28, 136 (1909).
[38] See Szivessy, Handbuch der Physik 21, 772–777 Julius Springer, (1929).
[39] Äckerlein, Phys. Zeits. 7, 594 (1906).
[40] Pauthenier, Ann. de Physique 14, 239 (1920); Jour. de Physique 2, 183 (1921).
[41] Larkin, Abs. Supplement J.O.S.A. and R.S.I. 19, 7 (1929).

The theory now usually accepted which seems to be in good agreement with most of the experimental results, began with the ideas of Kerr that the molecules of a substance were oriented by the electric field. However, Langevin[42] was the first definitely to formulate the theory although Larmor[43] and Cotton and Mouton[44] had already contributed materially to the fundamental concepts that he used. Langevin assumed that the molecules of a substance are both electrostatically and optically anisotropic and, as a result of the orientative action of the electric field upon the induced doublets in the molecules, the substance as a whole becomes doubly refracting. Born[45,46] extended the theory to include the effect of the orientative action of the electric field on the molecules due to the possible permanent electrical doublets. Recently, the phenomena have been investigated from the viewpoint of the new quantum mechanics.[47,48] In the case of dense fluids Raman and Krishnan[49] have modified the Langevin-Born theory by assuming that each molecule, in addition to being itself anisotropic, is also surrounded by an anisotropic polarization field or by an anisotropic distribution of polarizable matter. They suppose that this type of distribution arises from the alignment of the anisotropic molecules by the field.

We will first give a brief resumé of the Langevin-Born theory which is in good accord with the experimental data in gases. Starting from the well-known Lorentz-Lorenz relation[50,51,46] in an isotropic medium free from electrostatic fields

$$\frac{n^2 - 1}{n^2 + 2} = 4\pi N \alpha_0 / 3 = 4\pi N / 3 \frac{b_1 + b_2 + b_3}{3} \tag{7}$$

where n is the index of refraction, N the number of molecules per cm³, α_0 is the polarizability,† and b_1 b_2 b_3 are the moments induced in a molecule of the substance along its three principal axes by unit electrical force in the light wave acting along the three axes respectively. If now an electric field is applied to the medium, N changes by ΔN because of electrostriction while α_0 changes by $\Delta \alpha$ but the magnitude of $\Delta \alpha$ parallel to the lines of force is different from that in a direction at right angles thereto. To a sufficient degree of approximation Δn can now be found by differentiating Eq. (7)

[42] Langevin, Le Radium **7**, 249 (1910); C.R. **151**, 475 (1910).

[43] Larmor, Phil. Trans. 238 (1897); Aether and Matter **1**, 351 (1900).

[44] See Cotton and Mouton, C.R. **150**, 774 (1910); Ann. de Chem. et Phys. **8**, 19, 155 (1910); **8**, 20, 195 (1910).

[45] Born, Ann. de. Physik **55**, 177 (1918).

[46] See Debeye, Marx Handbuch der Radiologie, **6**, 754–776, Leipzig (1925).

[47] R. de L. Kronig, Zeits. f. Physik **45**, 458, 508 (1927); **47**, 702 (1928); Band Spectra and Molecules 117–120 Cambridge (1930).

[48] Born and Jordan, Elementare Quantenmechanik, 259–267, Julius Springer (1930).

[49] Raman and Krishnan, Proc. Roy. Soc. **A117**, 1, 589 (1927).

[50] Lorentz, Theory of Electrons 144, Leipzig (1909).

[51] Lorenz, Ann. d. phys. Chemie **11**, 70 (1880).

† The general formula for the polarizability α is

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT}.$$

$$\Delta n = \frac{(n^2 - 1)(n^2 + 2)}{6n}\left(\frac{\Delta N}{N} + \frac{\Delta\alpha}{\alpha_0}\right). \tag{8}$$

The electrostriction term can be obtained from thermodynamic reasoning.[52] It is

$$\frac{\Delta N}{N} = \frac{1}{4\pi}\left(\frac{\partial\epsilon}{\partial p}\right)_T \frac{E^2}{2} \tag{9}$$

where ϵ is the dielectric constant, p the pressure, and T the absolute temperature. As mentioned previously, the value for $\Delta\alpha$ is different parallel to the lines of force from that perpendicular to the lines of force. However, the derivation of $(\Delta\alpha)_p$ parallel and $(\Delta\alpha)_s$ perpendicular to the lines of force is rather long and laborious and, since treatments[45,53,54] can easily be found in the literature, we will merely write down the values here.

$$(\Delta\alpha)_p = 2(\Theta_1 + \Theta_2)\left(\frac{\epsilon + 2}{3}\right)^2\frac{E^2}{2}$$

$$(\Delta\alpha)_s = -(\Theta_1 + \Theta_2)\left(\frac{\epsilon + 2}{3}\right)^2\frac{E^2}{2} \tag{10}$$

where

$$\Theta_1 = \frac{1}{45kT}[(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)] \tag{11}$$

$$\Theta_2 = \frac{1}{45k^2T^2}[(\mu_1{}^2 - \mu_2{}^2)(b_1 - b_2) + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)] \tag{12}$$

where T is the absolute temperature, k the Boltzmann constant $b_1b_2b_3$, as before, in Eq. (7), the moments induced in a molecule along its three principal axes of optical anisotropy by unit electrical force in the light wave acting along the axes respectively and $a_1a_2a_3$ are the moments induced in the same directions respectively by unit electrostatic force arising from the applied electric field, while $\mu_1\mu_2\mu_3$ are the components of the permanent electrical moment along the same three directions. Since the change in the index of refraction is small in the Kerr electro-optical effect, we can find $(\Delta n)_p$ for the component of the light vibration parallel to the electric field by substituting Eqs. (9) and (10) in Eq. (8)

$$(\Delta n_p) = n_p - n = \frac{(n^2 - 1)(n^2 + 2)}{12n}\left[\frac{1}{4\pi}\left(\frac{\partial\epsilon}{\partial p}\right)_T + 2\left(\frac{\epsilon + 2}{3}\right)^2\frac{\Theta_1 + \Theta_2}{\alpha_0}\right]E^2 \tag{13}$$

and in a similar way for component of the light vibration perpendicular to the electric field

[52] Debye, Marx Handbuch der Radiologie 6, 750, 766, Leipzig (1925). See also Bruhat and Pauthenier, C.R. 186 1289 (1928).

[53] See Debye, Marx Handbuch der Radiologie 6, 760–767, Leipzig (1925).

[54] Szivessy, Handbuch der Physik 21, 743–763, Julius Springer (1929).

$$(\Delta n)_s = n_s - n = \frac{(n^2 - 1)(n^2 + 2)}{12n} \left[\frac{1}{4\pi} \left(\frac{\partial \epsilon}{\partial p} \right)_T - \left(\frac{\epsilon + 2}{3} \right)^2 \left(\frac{\Theta_1 + \Theta_2}{\alpha_0} \right) \right] E^2 \quad (14)$$

then

$$n_p - n_s = \frac{(n^2 - 1)(n^2 + 2)}{4n} \frac{\Theta_1 + \Theta_2}{\alpha_0} \left(\frac{\epsilon + 2}{3} \right)^2 E^2 \quad (15)$$

$$B \equiv B_m N = \frac{n_p - n_s}{\lambda E^2} = \frac{(n^2 - 1)(n^2 + 2)}{4n\lambda} \left(\frac{\epsilon + 2}{3} \right)^2 \frac{\Theta_1 + \Theta_2}{\alpha_0} \quad (16)$$

where B_m is the Kerr constant per molecule and λ is the wave-length of the light.

The treatment[47,48] of the Kerr electro-optical effect from the standpoint of the new quantum theory connects the magnitude of the electric double refraction with that of the Stark effect. The assumption is made that the parallel and perpendicular components of the Stark effect are intimately related to the refractive indices of light vibrations polarized parallel and perpendicular respectively to the electrical field. Born and Jordan derived an expression connecting the Kerr constant with the frequency of the light and temperature of the substance. They find

$$s_{0_p} - s_{0_s} = \frac{n}{2\pi}(n_p - n_s) = \frac{Bn\lambda E^2}{2\pi}$$

$$= K = E^2 \left(C_0 + \frac{1}{kT}(C_1 + D_0) + D_1/k^2 T^2 \right) \quad (17)$$

where s_{0_p} and s_{0_s} are the optical susceptibilities* parallel and perpendicular to the electrical field, k is the Boltzmann constant, and T the absolute temperature. C_0 and D_0 are determined by the changes in the quantum number "n" (which depends upon the relative position of the electrons in the molecule) while C_1 and D_1 are determined by the changes in the quantum number "J" (which depends upon the total angular momentum). It will be noted that Eq. (17) gives essentially the same variation with temperature as Eq. (16) if C_0 is very small. C_0 is probably quite small as it represents the contribution resulting from the anisotropy produced in the molecule itself by the field, i.e., this effect would exist in perfectly isotropic molecules. If this anisotropy produced in the properties of the molecule had been taken into consideration in the derivation of Eq. (16) and added to the intrinsically anisotropic properties of the molecule, a term in Eq. (16) independent of the temperature should have existed. However, experiment shows that such a term is probably very small in most cases and hence gives a justification for its neglect in Eq. (16).

As Kronig points out, although in some individual cases limited to gases an evaluation of B from the quantum mechanical expression Eq. (17) is possible in principle, it is not practicable because we do not as yet, at least, have sufficient knowledge concerning the Stark effect of the different transitions, especially those belonging to the continuous part of the spectrum. We shall,

* The optical susceptibility is given by the equation $s_0 = (n^2 - 1)/4\pi$.

therefore, discuss the experimental values from the viewpoint of the Langevin-Born theory.

(4) The Kerr electro-optical effect in gases

It is evident from the assumptions involved in the Langevin-Born theory that it should be expected to hold strictly only in cases where the mutual influence of the molecules is negligible or else definitely known. This condition is approximately realized in the case of gases and vapors, but our present knowledge of the liquid and solid states is in general notably insufficient for the purpose. Unfortunately the experimental data in the case of gases and vapors are comparatively meager, although a greater amount has accumulated for solids and liquids. This state of affairs results from the fact that the effect in gases and vapors at atmospheric pressure and below is comparatively small in comparison to that in liquids and solids and hard to measure with precision. However, where the data are available, the agreement between theory and experiment is as good as the accuracy of the latter will justify.

The first experimental work in gases and vapors in spectral regions removed from absorption lines was done by Leiser and Hansen[55,56] with the relative method of Des Coudres. Szivessy,[57] Stuart,[58] and others[59] have since obtained absolute measurements of B in several different gases. Table I gives some of the experimental values obtained together with some theoretical values obtained from Eq. (16) by evaluating its various terms by methods that will be described later. It will be observed that, in general, polar substances have the larger Kerr constants. Also it will be noted that the Kerr constant is intimately connected with the optical anisotropy of the molecules as measured by the depolarization factor r of the transversely scattered light (intensively studied by Rayleigh,[60] Raman,[61] Cabannes,[62] and others[63]), i.e., if the polarization of the light scattered at right angles to the direction of a beam of parallel light passing through a clean substance is examined, it is found to have, in addition to the strong component vibrating perpendicular to the incident ray, a relatively weak (in most substances) component vibrating parallel to the ray. The ratio of the weak to the strong component is indicated by r, from which the optical anisotropy* of the molecule can be computed.

[55] Leiser, Ver. d. deutsch Phys. Gesell **13**, 903 (1911); Phys. Zeits. **12**, 955 (1911).

[56] Hansen, quoted by Szivessy, Handbuch der Physik **21**, 739, Julius Springer (1929).

[57] Szivessy, Zeits. f. Physik **26**, 323 (1924).

[58] Stuart, Zeits. f. Physik **59**, 13 (1929).

[59] See Szivessy, Handbuch der Physik **21**, 724–790, Julius Springer (1929).

[60] Rayleigh, Proc. Roy. Soc. **A95**, 155 (1919); **97**, 435 (1920); **98**, 57 (1920).

[61] Raman, Molecular diffraction of light, Calcutta (1922).

[62] Cabannes, C. R. **160**, 62 (1915); **168**, 340 (1919); Ann. de Physique **15**, 5 (1921); Cabannes and Gauzit, Jour. de Physique **6**, 182 (1925).

[63] I. Rao, Ind. J. Phys. **2**, 61 (1927); See Gans, Wien-Harms, Handbuch der Experimental Physik **19**, 383 Leipzig (1928).

* The optical anisotropy is usually defined by the expression:

$$2\delta = \frac{(b_1-b_2)^2+(b_2-b_3)^2+(b_3-b_1)^2}{(b_1+b_2+b_3)^2} ; \delta = \frac{5r}{6-7r}$$

for a gas or vapor obeying Boyle's law.

TABLE I. *Values given by Raman and Krishnan[64] and by Sirkar[71].*

Gas or vapor	Depolariza-tion factor $r \times 100$	Approximate value $\mu \times 10^{18}$		Kerr constant per atmosphere for sodium D line at 20°C $B \times 10^{10}$	
		observed	calculated assuming $\rho = 0$	observed	calculated
Carbon dioxide	9.8	0	0	0.24 (17.5°C)	0.28
Nitrous oxide	12.2	0	0	0.48	0.48
Acetylene	4.6	0	0	0.29	0.23
Chlorine	4.1	0	0	0.35	0.30
Nitrogen	3.75	0	0		0.04
Oxygen	6.45	0	0		0.06
Carbon monoxide	3.4	0	0		0.05
Hydrogen chloride	1.0	1.03	1.04	0.90	
Methyl chloride	1.52	1.69	1.66	5.45	
Ethyl chloride	1.64	1.98	1.76	8.7	

Different investigators[64,65,66,67] have evaluated the Kerr constant B from the known magnitudes of the index of refraction, dielectric constant (electric moment) light scattering coefficient r, temperature, and density of the gas and the wave-length of the light. Also they have discussed the important bearing of the Kerr phenomena on molecular structure.

In order to derive the relation of the Kerr constant B to these other measurable quantities we substitute the value of the polarizability from Eq. (7) in Eq. (16). Then

$$B = \frac{\pi N (n^2 + 2)^2 (\epsilon + 2)^2}{27 n \lambda} (\Theta_1 + \Theta_2). \tag{18}$$

In the case of a gas or vapor at atmospheric pressure or below, (n^2+2) and $(\epsilon+2)$ are each approximately 3, so that Eq. (18) becomes

$$B = \frac{3\pi N}{\lambda} (\Theta_1 + \Theta_2) \tag{19}$$

and the problem reduces to the evaluation of Θ_1 and Θ_2.

For a nonpolar substance, μ_1, μ_2 and μ_3 are each zero, so that from Eq. (12) $\Theta_2 = 0$. The value of Θ_1 can be obtained from the depolarization factor r (which is known for a large number of substances), provided a_1, a_2 and a_3 in Eq. (11) can be expressed in terms of b_1, b_2 and b_3, since from the theory of light scattering

$$\frac{10r}{6 - 7r} \left[\frac{3(n - 1)}{2\pi N} \right]^2 = (b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2. \tag{20}$$

In order to express a_1, a_2 and a_3 in terms of b_1, b_2 and b_3 we adopt an as-

[64] Raman and Krishnan, Phil. Mag. **3**, 713–735 (1927).

[65] Stuart, Zeits. f. Physik **55**, 358 (1929).

[66] Wolf, Briegleb and Stuart, Zeits. f. phys. Chem. (B) **6**, 163 (1929).

[67] Brieglebo and Wolf, Lichtzerstreuung Kerreffekt und Molekülstrukture, Berlin, 1931.

sumption due to Gans[68] which seems most plausible and at the same time is justified by its success in giving a result in agreement with experiment.

$$\frac{a_1}{b_1} = \frac{a_2}{b_2} = \frac{a_2}{b_3} = \frac{\epsilon - 1}{n^2 - 1} \tag{21}$$

which gives upon substitution in Eqs. (11) and (16)

$$\Theta_1 = \frac{1}{45kT}\left(\frac{\epsilon - 1}{n^2 - 1}\right)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] \tag{22}$$

$$B = \frac{3(\epsilon - 1)(n - 1)^2}{4kT\pi N\lambda(n^2 - 1)}\frac{r}{6 - 7r} = \frac{3}{4\pi N\lambda kT}(\epsilon - 1)(n - 1)\frac{r}{6 - 7r}\text{app.} \tag{23}$$

which is the formula used for computing the values of B for the nonpolar gases in Table I.

In the case of polar molecules, μ_1, μ_2 and μ_3 are no longer zero, so that Θ_2 must be determined. In fact, the value of Θ_2 is usually much larger than Θ_1, so that any approximations made in Θ_1 do not appreciably effect the final result. In a polar gas or vapor, Θ_1 is obtained in the same way as in the nonpolar cases expect that the effect of the permanent dipoles in the molecules on the dielectric constant must be subtracted from the observed value when substituted in Eq. (21), i.e., in the ratio given in Eq. (21) the observed dielectric constant ϵ should be replaced by C where $\epsilon = C + a/T$. The value of C in the polar case and ϵ in the nonpolar case should be the same as the respective squares of the indices of refraction extrapolated to infinite wave-length. To evaluate Θ_2 it is necessary to know not only the relative magnitude of b_1, b_2 and b_3 but also the angles that they make respectively with μ; i.e. we must know both the "optical ellipsoid" of the molecule and the relative position and magnitude of the permanent electric moment μ. The magnitude of the permanent moment is usually obtained from dielectric constant measurements[69] while information concerning the optical shape of the molecule is obtained from measurements[61,62,63] of the factor of depolarization r of the transversely scattered light. The optical shape of the molecule is in general not necessarily simple but we will limit ourselves to cases where it can be approximately represented by an ellipsoid with three principal axes. With this information available, the Kerr constant itself gives the position of the permanent electrical moment with reference to the three principal axes of the optical ellipsoid. Following Raman and Krishnan[64] we will consider the simple cases where the optical ellipsoid is a spheroid of revolution. Let us assume that $b_2 = b_3$ and that μ makes an angle ρ with the axes along b_1. Then by projection $\mu_1^2 = \mu^2 \cos^2\rho$ and $\mu_2^2 + \mu_3^2 = \mu^2\sin^2\rho$. Substituting these values

$$\Theta_2 = \pm\frac{(n - 1)\mu^2}{30\pi N k^2 T^2}(2\cos^2\rho - \sin^2\rho)\left(\frac{5r}{6 - 7r}\right)^{1/2} \tag{24}$$

[68] Gans, Ann. d. Physik 65, 97 (1921).

[69] See Debye, Polar molecules, Chemical Catalogue Co. (1929).

where the $+$ sign is taken in the case where $b_1 > b_2 = b_3$ and the $-$ sign where $b_1 < b_2 = b_3$. As mentioned previously, Θ_2 in polar substances is usually much larger than Θ_1, so that when $b_1 < b_2 = b_3$ and Θ_2 negative it is clear from Eqs. (18) and (19) that B is also negative. Physically a negative value of B means that the permanent electrical moment lies along (or makes a small angle with) the axes of minimum optical polarizability. Hence with the application of the electric field, since the permanent electrical moment is supposed fixed with respect to the optical ellipsoid, the molecules are rotated so that the axes of smaller optical polarizability is along the lines of force. As a result n_s is greater than n_p and B becomes negative. It is only in the case of polar substances that a negative B should occur, unless the assumption is made that the direction of greatest electrostatic polarizability in the molecule is the same as that of the smallest optical polarizability, which would conflict with the usually accepted ideas of electrical and optical anisotropy.[46,68,70] It might be noted here that the theory of Langevin which took into account only the induced moments could not account for negative Kerr constants, but with the modifications introduced by Born taking into account the effect of the permanent electrical moment, the negative Kerr constants became a logical consequence of the theory. The presence of negative Kerr constants strikingly confirms the usual idea that the permanent moment in many substances may be very much greater than a possible induced moment. In nonpolar substances where $\Theta_2 = 0$, a negative B has never been observed, which in itself is good evidence for the general validity of the assumptions made in the Langevin-Born theory.

As previously mentioned, one of the valuable uses of Eq. (24) is that it furnishes an easy way in simple molecules of finding the angle ρ made by the permanent electrical moment and the direction of the principal axes of the optical ellipsoid, provided μ_1, r and B are known. For example Raman and Krishnan show that in the case of HCl the angle $\rho = 0$, while in CH_2Cl_2 $\rho = \pi/2$. Sirkar[71] and others[58,72] have shown that in some substances ρ may have other values. Where the angle ρ equals zero, $\pi/2$, or is definitely known, it is clear that the permanent electrical moment can be determined from the known values of the Kerr constant and r with considerable precision since μ enters into Eq. (24) as a higher power than either B or r. When the Kerr constant B, the permanent electric moment μ, the factor of depolarization r of the scattered light, the index of refraction n, the dielectric constant ϵ, and the general shape of the optical ellipsoid, are all known it is possible to find the actual values of b_1, b_2 and b_3; i.e. since Θ_1 can be obtained from Eq. (22) in the way described above for polar substances, the expression

$$[(\mu_1{}^2 - \mu_2{}^2)(b_1 - b_2) + (\mu_2{}^2 - \mu_3{}^2)(b_2 - b_3) + (\mu_3{}^2 - \mu_1{}^2)(b_3 - b_1)]$$

is given in terms of•the known Kerr constant B by Eqs. (12), (18), and (19). Now if the angles made by the permanent electric moment and the three

[70] Bragg, Proc. Roy. Soc. A105, 370 (1924); 106, 346 (1924).

[71] Sirkar, Ind. J. Phys. 3, 209 (1928).

[72] Stuart, Zeits. f. Physik 63, 533 (1930); Phys. Zeits. 31, 616 (1930).

principal axes of the optical ellipsoid are known, then the magnitudes. of $\mu_1\mu_2\mu_3$ are obtained. Hence the value of a linear function of $b_1b_2b_3$ is given by the known magnitude of B. For example in the simple case where μ coincides with μ_1, $\rho = 0$ and $\mu_2 = \mu_3 = 0$, the above function reduces to $(2b_1 - b_2 - b_3)\mu^2$ and is expressed by Eqs. (18) and (19) in terms of B, n, ϵ and r. Further, it is possible to evaluate the expression $(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2$ from the known values of r and n by Eq. (20), while $b_1 + b_2 + b_3$ is given by Eq. (7). Therefore, from the three different equations expressing $b_1b_2b_3$ in terms of known quantities, the possible valuesof $b_1b_2b_3$ can be obtained. Stuart[65],[72] has computed these values in a few cases where the data are available and indicated their use in the study of the structure of the molecules. With the values of b_1, b_2 and b_3 known the assumption of Gans, Eq. (21) gives a_1, a_2 and a_3 directly.

The variation of B with temperature has been studied in several gases and vapors[72],[31] and found to be in general accord with the theory. The experimental data, however, are so scanty that no further conclusion should definitely be drawn.

The variation of B with wave-length has also been studied in gases and vapors but again the data are so meager that no definite conclusion should be drawn. It is indicated, however, that Havelock's formula Eq. (5) holds approximately over the visible range. It will be remembered that Havelock derived his formula Eq. (5) on a rather special hypothesis and before the Langevin-Born theory was proposed, but if the value of (n^2+2) from Eq. (7) is substituted into Eq. (16)

$$B = \frac{(n^2 - 1)^2}{n\lambda} \frac{3}{16\pi N\alpha_0^2} \left(\frac{\epsilon + 2}{3}\right)^2 (\Theta_1 + \Theta_2) \tag{25}$$

or

$$B \propto \frac{(n^2 - 1)^2}{n\lambda} \quad \text{(Havelock's law)} \tag{26}$$

provided α_0, ϵ, Θ_1 and Θ_2 are independent of λ.

In a few cases, notable in sodium vapor, "an anomalous" Kerr electro-optical effect has been observed in the immediate region of an absorption line or band.[73],[74] This is, of course, what should be expected[75] from theory since the index of refraction also shows the well-known "anomalous effects" in these regions.[76] Kopfermann and Ladenburg have related their results obtained in sodium vapor in the region near the D lines to the Stark effect components of the lines D_1 and D_2 and obtained a fair correlation considering the assumptions it was necessary to make.

The measurement of the variation of B with increased density of the gas has also led to considerable experimental difficulty. The increased pressure

[73] Kopfermann and Ladenburg, Ann. d. Physik **78**, 659 (1925).

[74] Bramley, Jour. Frank. Inst. **205**, 539 (1928).

[75] See Herzfeld, Ann. d. Physik **69**, 369 (1922).

[76] See Wood, Physical Optics, pp. 113 and 422.

necessary to produce an increase of density inside the Kerr cell produces so many strains in the windows that precise measurements of the double refraction were made almost impossible, nevertheless Szivessy[54,77] measured B in CO_2 up to three atmospheres with considerable precision and found over this small range that the Kerr effect per molecule did not change. Lyon[78] worked in CO_2 up to 78 atmospheres and came to the conclusion that the Kerr effect per molecule did not change over the range from 10 to 50 atmospheres. Recently[81] however, by placing the polarizing and analyzing apparatus inside the Kerr cell it was found possible to study B up to hundreds of atmospheres pressure with precision. The nonpolar CO_2 was investigated up to 0.18 gm/cm at just above the critical temperature and found to exhibit a very slight change in B with increase of density. This, however, was in accord with the theory, for when the indices of refraction[79] and the dielectric constants[80] for CO_2 at the respective densities were substituted in Eq. (18), such a variation of the Kerr effect per molecule as observed should be expected. Since B can be measured with considerable precision at high pressures, it may serve as a powerful auxiliary in finding how the molecules influence each other as they are brought closer together on the average.

In the writer's opinion there is an urgent need for more good experimental data on the Kerr effect in both polar and nonpolar gases and vapors including its variation with wave-length of the light, temperature, and density of the gas. If possible, the electro-optical dispersion should be studied in detail from the infrared to the ultraviolet including regions near absorbtion bands, while the density and temperature should be varied over ranges great enough to carry the substance from the gaseous state where the molecules are far enough apart to be mutually independent, into the liquid state. With these data at hand our hypothesis concerning the electrical and optical anisotropy of the individual molecules can be rigidly tested. Also an insight into how they interact with each other in forming a liquid will be obtained.

(5) The Kerr electro-optical effect in liquids

The Kerr electro-optical phenomena in liquids compared to that in gases and vapors is easier to investigate experimentally but is more difficult to interpret quantitatively. This latter situation probably arises from our present lack of complete knowledge concerning the liquid state for, as pointed out previously, where the data are available in the case of gases, there is quantitative agreement. Nevertheless, in general the theory is in qualitative accord with experimental data and, in a few cases, in fair quantitative agreement. In fact, the characteristics of the effect are correlated so well by the theory as to give assurance to the belief that, in the main, its use is justified. The experimental data in the case of liquids, although considerably more abundant than in the case of gases and vapors, are still entirely too scanty to

[77] Szivessy, Zeits. f. Physik **26**, 338 (1924).
[78] Lyon, Zeits. f. Physik **28**, 287 (1924).
[79] Phillips, Proc. Roy. Soc. **A97**, 225 (1920).
[80] Keyes and Kirkwood, Phys. Rev. **26**, 754 (1930).

give much more than a bare outline of the more prominent features of the phenomena. In many cases, especially in conducting liquids and where the fluids are easily contaminable, the experimental values may be quite appreciably in error. A striking example of this is illustrated by the recent work of Illberg,[81] Möller,[82] Hehlgans[83] and others[84] on nitrobenzene, where large apparent variations in the experimental values of B are brought about by impurities. As in gases and vapors the general rule is that the Kerr effect is larger in polar than in nonpolar liquids. As a matter of fact, the effect of the permanent moment μ is more prominent in liquids than in gases or vapors; an observation naturally in accord with Eq. (16) since $(\epsilon+2)^2$ is one of its factors. In general the Kerr effect per molecule is larger in gases and vapors than in liquids but there are some remarkable exceptions. Raman and Krishnan[49] have modified the Langevin-Born theory in a way that will explain this difference in B per molecule in dense fluids, but we shall postpone their treatment until after briefly outlining the theory following that given for gases and vapors; i.e., the assumption will be made for the time being that each molecule, although itself anisotropic, is surrounded by an isotropic distribution of polarizable matter.

Starting from Eq. (18), we must evaluate Θ_1 and Θ_2 from quantities that can be determined experimentally. The nonpolar case will be attempted first because it is simpler, since $\Theta_2 = 0$. As in the case of a gas, it is necessary at present to express the electrical constants of the molecule $a_1 a_2 a_3$ in terms of the optical constants $b_1 b_2 b_3$, since the latter can be determined from light scattering experiments. With the assumptions of Gans,

$$\frac{a_1}{b_1} = \frac{a^2}{b^2} = \frac{a^3}{b^3} = \frac{\epsilon - 1}{\epsilon + 2} \Big/ \frac{n^2 - 1}{n^2 + 2} \tag{27}$$

and substituting into Eq. (11)

$$\Theta_1 = \frac{1}{45kT} \frac{(\epsilon - 1)(n^2 + 2)}{(\epsilon + 2)(n^2 - 1)}[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]. \tag{28}$$

The relation expressing r in terms of the optical constants in a liquid is somewhat uncertain and different relations[85] have been proposed; but as the present theory is only approximate we are perhaps justified in using[86]

$$r = \frac{6[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]}{10(kT\beta N)(b_1 + b_2 + b_3)^2 + 7[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]} \tag{29}$$

where β is the isothermal compressibility of the liquid and $b_1 + b_2 + b_3$ is given by the well-known relation[46] in Eq. (7)

[81] Illberg, Phys. Zeits. **29**, 670 (1928).

[82] Möller, Phys. Zeits. **30**, 20 (1929); **32**, 697 (1931).

[83] Hehlgans, Phys. Zeits. **30**, 942 (1929); **32**, 718 (1931).

[84] Dillon, Zeits. f. Physik **61**, 386 (1930); Lohaus, Phys. Zeits. **27**, 217 (1926).

[85] Krishnan, Proc. Ind. Asso. Sci. **9**, 251 (1926).

[86] Raman and Krishnan, Phil. Mag. **3**, 727 (1927).

$$\Theta_1 = \frac{9\beta(\epsilon - 1)(n^2 - 1)}{8\pi^2 N(\epsilon + 2)(n^2 + 2)} \cdot \frac{r}{6 - 7r} \tag{30}$$

and Eq. (17) becomes

$$B = \frac{\beta(n^2 - 1)(n^2 + 2)(\epsilon - 1)(\epsilon + 2)}{24\pi n\lambda} \cdot \frac{r}{6 - 7r} . \tag{31}$$

This formula has been used by Raman and Krishnan[86] to compute B for several nonpolar liquids and, although the theroetical values are in general of the same order of magnitude as the experimental values, there exist deviations in excess of the errors of the experimental quantities involved.

In polar liquids Θ_1 can be approximately evaluated in the same way as in the nonpolar case, except that instead of substituting the observed ϵ in Eq. (27) the square of the index of refraction extrapolated to infinite wave-length is used. On the other hand, Θ_2 is much harder to determine because it is necessary to know the shape of the optical ellipsoid and the magnitude of the electric moment. It is well known that the latter[87,88] in dense fluids, is not the same as in the vaporous state but that μ assumes a sort of "effective value" indicating that molecular interaction influences the electric moment. Also, there is reason to believe that the optical shape found suitable in the gaseous state is effectively distorted in the liquid state.[89,90,91] These changes in the effective optical ellipsoid and the effective electric moment are especially large in the so-called associated liquids. Therefore, we are not justified in using μ and the constants of the optical ellipsoids as determined from the vaporous state in evaluating B in the liquid state. This conclusion is also amply demonstrated by the deviations between the experimental values of B and those derived theoretically from the constants in the state of gas or vapor. However, it should be possible to compute B in the liquid state if we know the nature and extent of the molecular interaction, for it is possible to measure both r and the effective μ in the liquid state. Also, from a study of x-ray scattering from liquids,[92,93,94,95,96] information as to the size and grouping of the molecules can be obtained. Further, the changes in the index of refraction and the dielectric constant have been traced from the gaseous to the liquid state in a few cases.

It would seem plausible that any theory which accounts for the changes in the Kerr constant B in passing from the gaseous to the liquid state should

[87] Debye, Polar Molecules, 36–58 Chem. Cat. Co. (1929).

[88] Smyth, Dielectric Constant and Molecular Structure, Chem. Cat. Co. (1931).

[89] Raman and Krishnan, Phil. Mag. **5,** 498 (1928); Krishnan, Proc. Roy. Soc. **A126,** 155 (1929).

[90] S. Rao, Ind. J. Phys. **2,** 7, 179 (1927–28); **3,** 1 (1928).

[91] I. Rao, Ind. J. Phys. **2,** 61 (1927).

[92] Debye and Scherrer, Nachr. Gött-Akad. **16,** (1916).

[93] Stewart and Marrow, Phys. Rev. **30,** 232 (1927).

[94] Sogani, Ind. J. Phys. **1,** 357 (1927); **2,** 97 (1928).

[95] Krishnan and Rao, Ind. J. Phys. **4,** 39 (1929).

[96] See Stewart, Rev. Mod. Phys. **2,** 116 (1930).

also account for the corresponding changes in r as well as deviations from the Clausius-Mosotti and Lorentz-Lorenz relations. From time to time special hypotheses have been proposed to account for individual variations of these, but perhaps the most satisfactory general theory is that proposed by Raman and Krishnan.[49] Therefore, we shall briefly outline this theory for the Kerr effect and indicate how it applies. Raman and Krishnan suppose that not only the molecule itself is anisotropic, but that it is surrounded by an anisotropic distribution of polarizable material, i.e. they modify the Langevin-Born hypothesis by assuming that the polarization field surrounding a molecule in a liquid is anisotropic instead of isotropic. They imagine this anisotropic distribution in the immediate vicinity of the molecule to be brought about by the orientation of the surrounding anisotropic molecules. With these assumptions they obtain an expression for the Kerr constant B which we will merely write down, and refer the reader to the original paper for a detailed derivation.

$$B = \frac{n^2 - 1}{4n\lambda} \frac{3}{\alpha_0}(\Theta_1' + \Theta_2') \tag{32}$$

where

$$\Theta_1' = \frac{1}{45kT}[(A_1 - A_2)(B_1 - B_2) + (A_2 - A_3)(B_2 - B_3) + (A_3 - A_1)(B_3 - B_1)] \tag{33}$$

$$\Theta_2' = \frac{1}{45k^2T^2}[(B_1 - B_2)(M_1^2 - M_2^2) + (B_2 - B_3)(M_2^2 - M_3^2)$$
$$+ (B_3 - B_1)(M_3^2 - M_1^2)] \tag{34}$$

where

$$A_1 = a_1(1 + p_1s_e)^2 \qquad B_1 = b_1(1 + q_1s_0)$$
$$A_2 = a_2(1 + p_2s_e)^2 \qquad B_2 = b_2(1 + q_2s_0)$$
$$A_3 = a_3(1 + p_3s_e)^2 \qquad B_3 = b_3(1 + q_3s_0)$$
$$M_1 = \mu_1(1 + p_1s_e) \qquad M_2 = \mu_2(1 + p_2s_e) \qquad M_3 = \mu_3(1 + p_3s_e)$$

where s_0 and s_e are the optical and electrical susceptibilities respectively, while $p_1p_2p_3$ and $q_1q_2q_3$ are called the polarization constants of the electrostatic field and the field of the light wave respectively along the three axes, and the other quantities have the same meaning as in Eqs. (11), (12) and (16). It is clear that when

$$p_1 = p_2 = p_3 = q_1 = q_2 = q_3 = 4\pi/3$$

as in an isotropic distribution around a molecule, Eq. (32) reduces to Eq. (16). From the same theory[97,95] the factor of depolarization of the scattered light in a liquid is shown to be

$$r = \frac{6nN[(B_1 - B_2)^2 + (B_2 - B_3)^2 + (B_3 - B_1)^2]}{90\left(\frac{n^2 - 1}{4\pi}\right)^2 RT\beta + 7nN[(B_1 - B_2)^2 + (B_2 - B_3)^2 + (B_3 - B_1)^2]} \tag{37}$$

[97] Raman and Krishnan, Phil. Mag. 5, 498 (1928).

In order to evaluate the Kerr constant from the above theory it is necessary to determine the A's and B's in the nonpolar case and the M's in addition in the polar case. Considering the simple non polar case where $b_2 = b_3$, the b's can be determined by the values of r and n in the vapor state. Then from the assumption of Gans the a's are determined. The evaluation of the p's and q's is in general very difficult, but with the aid of certain assumptions they can be calculated approximately for special cases. For the purpose of calculation, the anisotropy of the polarization field can be represented with sufficient approximation by a surface charge on an ellipsoidal cavity surrounding the molecule. It is supposed that the distribution of polarizable matter surrounding this ellipsoidal cavity is isotropic and that the shape of this cavity (into which other molecules cannot enter) is determined by the shape of the molecule. Therefore, the polarization field produced at the center is equal to the field produced by a surface charge $-SE\cos\Theta$ per unit area of the ellipsoid, where the normal makes an angle Θ with E. Now for illustration, assume the shape of the cavity is a prolate spheroid with semi-axes $b = c = a$ $(1 - e^2)^{1/2}$ where e is the eccentricity, then the polarization constants can be computed from the well-known equations[98,49]

$$p_1 = q_1 = 4\pi\left(\frac{1}{e^2} - 1\right)\left(\frac{1}{2e}\log\frac{1 + e}{1 - c} - 1\right)$$

$$p_2 = p_3 = q_2 = q_3 = 2\pi\left(\frac{1}{e^2} - \frac{1 - e^2}{2e^2}\log\frac{1 + e}{1 - e}\right)$$

(38)

which can be evaluated if a, b and c are known. Fortunately, from the data on the scattering of x-rays by the liquids, approximate values for these semi-axes can be obtained,[95] so that the Kerr constant B can be evaluated. The influence of the anisotropy of the polarization field computed in this way is well illustrated by the results for pentane, for which by the above calculations $B = 5.5 \times 10^{-9}$, while by the Langevin-Born theory assuming the p's and q's all equal, $B = 17.9 \times 10^{-9}$. The experimental value is $B = 5.0 \times 10^{-9}$, in fair accord with that given by the Raman-Krishnan theory. It will be observed that in this case of pentane the influence of the anisotropy of the polarization field is such as to reduce the effective double refraction. This is a quite general rule and holds in cases free from liquid "associations". The above theory of Raman and Krishnan is found to be in at least good qualitative agreement with experiment in cases where it has been applied, and is certainly better than the Langevin-Born theory for dense liquids.

The temperature variation of the Kerr constant in liquids

It will be recalled that the electrical double refraction is believed to arise from the result produced by the orientative influence of the applied electric field on the induced and permanent electrical moments in the anisotropic molecules. This alignment of the molecules by the field is constantly opposed by the thermal agitation, so that as the temperature is raised, the col-

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[98] See Maxwell, Electricity and Magnetism, 3rd ed. Clarendon, p. 69 (1892).

lisions between molecules becoming more numerous and violent, the amount of alignment of the molecules is decreased. The magnitude of the Kerr electro-optical effect, therefore, should decrease with increasing temperature. The temperature variation of B has been studied in several liquids by many different investigators[99-107] with the indication that the experimental values are in fair accord with what should be expected from theory. In fact the temperature variation of B, together with the observed changes in the x-ray scattering with the electric field on and off, are among the best evidence that we have of the orientation of molecules actually taking place.[108]

In nonpolar liquids the temperature variation of B is usually less than in polar liquids, a result in agreement with the fact that T enters into Eqs. (11) and (33) as the inverse first power and into Eq. (12) and (34) for Θ_2 (which is zero in the nonpolar case) as the inverse second power. Recent measurements of the variation with temperature of the depolarization factor r for the transversely scattered light, shows that this quantity per molecule usually increases with temperature. From this, it is concluded that the anisotropy of the molecule itself remains almost constant but that the effective increase of the anisotropy of the substance with temperature is brought about by a decrease in the anisotropy of the polarization field produced by the surrounding molecules. From the preceding theories a decrease in the anisotropy of the polarization field increases the Kerr effect so that a careful study of the variation of B with temperature should give information on how this anisotropic polarization field varies. Indeed, most of the experimental results show that the observed variation of B with temperature is actually greater than the values computed from Eq. (16), in which equation the polarization field is considered isotropic and hence invariable. It should be noted in passing that nitrobenzene is one of the exceptions to the above statement. Moreover, it is not only peculiar in this respect to B but to r as well, indicating probable molecular association. It is also unique in possessing one of the largest known Kerr constants in the visible region. There is need for more good data on the variation of B with temperature in many liquids.

The variation of B with wave-length of the light

Kerr as early as 1892 observed a variation in the magnitude of the electrical double refraction in liquids with wave-length, but precise quantitative data were not available until the work of Blackwell[109] and McComb.[14] These

[99] Quincke, Wied. Ann. **19**, 745 (1883).
[100] Schmidt, Ann. d. Physik **7**, 142 (1902).
[101] Cotton and Mouton, C. R. **150**, 774 (1910).
[102] Bergholm, Ann. d. Physik **51**, 414 (1916); **65**, 128 (1921).
[103] Szivessy, Zeits. f. Physik **2**, 30 (1920).
[104] Lyon and Wolfram, Ann. d. Physik **63**, 739 (1920).
[105] Raman and Krishnan, Phil. Mag. **3**, 769 (1927).
[106] Kürten, Phys. Zeits. **32**, 251 (1931).
[107] See Szivessy, Handbuch der Physik **21**, 769 (1929).
[108] McFarlan, Phys. Rev. **35**, 1469 (1930).
[109] Blackwell, Proc. Amer. Acad. **41**, 647 (1906).

investigators found that Havelock's law Eq. (26) was in excellent accord with the observed values. Later workers[110] have also agreed that over the visible range this law of Havelock's is in harmony with the facts. However, in some recent work of Szivessy and Dierkesmann,[111] in which they investigated the phenomena over both the visible and ultraviolet ranges, they conclude that the course of the electro-optical dispersion curve is not exactly given by the formula of Havelock. Ingersoll[112] has recently started an important investigation of the Kerr electro-optical effect in the infrared and finds in CS_2, from 0.5μ to 2μ, that Havelock's formula is verified. The study of this electro-optical dispersion is of considerable interest because it designated the quantities entering into Eqs. (16) and (32) that are independent of the wavelength of the light. For example, if Havelock's law holds over a certain range of wave-lengths, then Eq. (25) shows that α_1, ϵ_1, Θ_1 and Θ_2 are independent of λ over this range, or vary in such a way as to always give complete compensation.

Absolute values of n_p and n_s

The question arose early as to the absolute value of the refractive indices for light vibrations parallel to the lines of force n_p and perpendicular to the lines of force n_s respectively. The experimental methods previously described, which measure the magnitude of the double refraction, could determine $n_p - n_s$ but not n_p or n_s. The general method of measuring the absolute value of these indices of refraction has been to place a Kerr cell in one of the arms of an interferometer (Michelson, Jamin, etc.) so that the light passing through could be plane polarized either parallel or perpendicular to the lines of force. In the other arm of the interferometer a glass cell filled with the same liquid and having the same optical length was so arranged that the light path through it was in a field free space. This is necessary, of course to make it possible to use white light "fringes" for reference if desired. When the field was applied to the Kerr cell the "shift in the fringes", first with the plane of vibration of the polarized light parallel and second perpendicular to the lines of force, gave a measure of $n_p - n$ and $n - n_s$. Since n could be measured independently, n_p and n_s could be obtained.

From Eq. (6) it will be seen that Havelock derived the expression $(n_p - n_s)/(n_s - n) = -2$. Voigt,[113] from his theory which assumes that the electric double refraction arises from a modification of the interatomic and intermolecular forces by the field rather than an orientation of the molecules, derived the formula $(n_p - n)/(n_s - n) = 3$. In generalizing this theory Enderle[114] found the above expression to depend upon λ and to approach $+3$ for frequencies that are small compared with those of the electrons. By dividing Eq. (13) by Eq. (14) it will be seen that Havelock's Eq. (6) is obtained on

[110] See Szivessy, Handbuch der Physik **21**, 772–780.
[111] Szivessy and Dierkesmann, Ann. d. Physik **3**, 507 (1929).
[112] Ingersoll, Phys. Rev. **37**, 1184 (1931).
[113] Voigt, Lehrbuch der Optik 352 (1900).
[114] Enderle, quoted by Mouton, Int. Crit. Tab. **7**, 112.

the Langevin-Born theory provided the electrostriction terms are neglected. However, these electrostriction terms are not usually small enough to be neglected in comparison with the others, so that Eq. (6) should not necessarily hold for steady applied fields. Nevertheless, the electrostriction usually requires a longer time to be established than the Kerr electro-optical effect after the application of the electric field, so that it is possible experimentally to measure $n_p - n$ and $n_s - n$ before electrostriction develops. This procedure also makes it possible to eliminate the heating of the liquid, which is always a troublesome factor in these measurements. Experiments of this kind, performed by several different investigators,[39,40,41] have shown that Eq. (6) is approximately correct.

(6) The relaxation time of the Kerr electro-optical effect

In his first experiments, which were made with glass, Kerr observed that the double refraction required several seconds to reach full value or completely to disappear after the electric field was applied or removed, respectively. However, in his experiments with liquids he was unable to detect any time-lag of the Kerr effect behind the electric field. Later Blondlot[115] showed that any existing time lag of the Kerr effect in liquids that he studied was less than 2.5×10^{-5} sec., while Abraham and Lemoine[116] came to the conclusion that in CS_2 the Kerr effect did not remain as long as 10^{-8} sec. after the electric field was relaxed. Since that time other experimenters[117,118] have interpreted their results as indicating time lags from 10^{-8} to 10^{-10} sec. in different liquids, such as CS_2 and nitrobenzene. However, Professor Lawrence and the writer,[119,120] after a series of investigations, have concluded that there is, at least, no experimental evidence of time lags in the Kerr effect for liquids with comparatively small molecules and low viscosities. Recently, Ranzi[121] has also arrived at essentially the same conclusion. On the other hand, in the case of viscous liquids, that are at the same time polar, time lags of considerable length have been observed.[122,123,124] Raman and Sirkar, the first to observe these long time lags in viscous liquids, found, by applying a rapidly oscillating electric potential to a Kerr cell filled with octyl alcohol, which has a negative Kerr constant B, that the electric double refraction first decreased with increase of frequency of the applied electric field to the Kerr cell until it completely disappeared, then reappeared and increased with still higher frequency of the applied electric field. Sirkar[124] found that in undecyl alcohol the time lag of the Kerr effect lies between 10^{-8} and 10^{-9} sec.

[115] Blondlot, Jour. de Physique (2), 7, 91 (1888).

[116] Abraham and Lemoine, C. R. 129, 206 (1899); 130, 499 (1900); Jour. de Physique (3) 9, 262 (1900).

[117] James, Ann. d. Physik 15, 954 (1904).

[118] Gutton, Jour. de Physique (5) 2, 51 (1912); (5) 3, 206 (1913); 3, 445 (1913).

[119] Lawrence and Beams, Phys. Rev. 32, 478 (1928).

[120] Beams and Lawrence, Jour. Frank. Inst. 206, 169 (1928).

[121] Ranzi, N. Cimento 7, 270 (1930).

[122] Raman and Sirkar, Nature 121, 794 (1928).

[123] Kitchin and Müller, Phys. Rev. 32, 979 (1928).

[124] Sirkar, Ind. J. Phys. 3, 409 (1928).

Experiment shows that, as a rule, the Kerr constant is larger in polar than in nonpolar liquids and hence Θ_1 is usually small compared to Θ_2 in polar liquids. Moreover, if such were not the case it would be difficult satisfactorily to explain the existence of negative Kerr constants on the Born-Langevin-Raman and Krishnan theory. That is, the contribution to the Kerr effect of the anisotropic polar molecules oriented by the couple exerted on their permanent electric moments by the electric field is much greater than that resulting from the alignment produced by the couple exerted on their induced doublets by the field. Debye[125] has derived a formula by which it is possible to determine the time t required for the moments to revert to random distribution after the removal of the impressed electric field. When the molecules are spherical he finds

$$t = \frac{4\pi\eta a^3}{kT} \tag{39}$$

where η is the coefficient of viscosity, a the radius of the molecule, k Boltzmann's constant, and T the absolute temperature. Although Eq. (39) is rather approximate because of the simplifying assumptions that the molecules are spherical and that Stokes law holds for particles as small as molecules, it does give the right order of magnitude for t and shows how it should vary with increasing η and a. It is also apparent that if the electric field is applied and removed quickly enough the Kerr effect should decrease and almost vanish. Indeed, if the liquid has a negative Kerr constant and is placed in a rapidly oscillating electric field, the negative double refraction which is due to the orientation produced by the electric field on the permanent dipoles in the molecules decreases to zero with increase of frequency, while the contribution to the Kerr effect, usually positive, resulting from the influence of the field on the induced doublets need not change so much. According to Raman and Sirkar, in negative liquids the Kerr effect first should decrease with frequency of the applied field, pass through zero, and increase again just as they observed in octyl alcohol, i.e., the electric double refraction can pass from negative to positive with increase of frequency of the field.

Bramley[126] has reported some curious phenomena produced in water at certain high frequencies of the impressed oscillating electric field. At first he thought that an increased Kerr effect existed at these frequencies, but has since been led to a different conclusion. He discovered that certain lines of the spectrum had their wave-length shifted toward the red in passing through his oscillating Kerr cell and that the light was intensely scattered. Recently he has explained the phenomenon as due not to the Kerr effect at all, but to the scattering of light by the changes in the salt content of the water. Sirkar[124] also noticed a peculiar phenomenon in the higher alcohols which became most conspicuous in the regions of frequencies where strong electric absorption occurred. The liquids became translucent in the fields at such frequencies and

[125] Deybe, Polar Molecules 83, Chem. Cat. Co. (1929); Marx Handbuch der Radiologie 646, 773 Leipzig (1925); Tummers, Diss. Utrecht 1914 (quoted by Debye).

[126] Bramley, Jour. Frank. Inst. **206**, 151 (1928); **207**, 316 (1929); Phys. Rev. (A) **33**, 279 (1929); **34**, 1061 (1929).

restored the light between crossed nicols. The nature of the phenomenon has not been definitely explained but, as he points out, the indications are that it also results from a kind of scattering rather than the Kerr effect.

The extremely short time lag of the electric double refraction behind the electric field in the Kerr electro-optical effect in nonviscous liquids with small molecules, has been utilized in many investigations in different fields. The Kerr cell used between crossed nicols, as in Fig. 1 for example, gives an excellent light shutter which responds almost instantaneously to electrical control. Light flashes as short as 10^{-9} sec. have been produced by means of Kerr cells, and phenomena taking place in times of the order of 10^{-8} sec. have been observed by their use. Reviews[127,128] of the use of Kerr cells for the measurements of time intervals and the production of flashes of light, together with extended bibliographies, already exist in the literature so we shall not describe further the various uses of the phenomenon.

(7) Miscellaneous

The Kerr electro-optical effect in liquid mixtures has not been extensively studied, but the existing data[129,130] indicate that the amount of electric double refraction cannot be computed directly from the percentage mixture and the known values of the Kerr constants for the pure substances in all cases. Investigations of the Kerr effect in mixtures are of interest because it is possible, by extrapolating the graph of the Kerr constant versus concentration to very weak dilutions, to determine the effective Kerr constant per molecule not only when each molecule is surrounded by similar molecules but by different molecules as well. Of particular importance are the results obtained when the liquid under investigation is dissolved in a normal nonpolar liquid with a very small Kerr constant, i.e., when each anisotropic molecule of the liquid under investigation is practically surrounded by molecules possessing small anisotropy.* If the molecules of the solvent were isotropic, or nearly so, the theory of Raman and Krishnan would indicate that, in dilute solution, the Kerr constant per molecule would increase and approach that predicted by the Langevin-Born theory. The electric double refraction in optically active substances and in their mixtures has been investigated quite extensively especially by R. de Mallemann,[131] who also discusses the theory in detail.

The Kerr electro-optical effect per molecule of solids can also be investigated by dissolving the solid in liquids with small Kerr constants. There is need for more experimental work on the Kerr effect in mixtures, for it seems likely that such investigations will throw additional light on intermolecular actions.

Investigations of the double refraction produced by the orientation of

[127] Kingsbury, Rev. Sci. Inst. **1**, 22 (1930).

[128] Beams, Rev. Sci. Inst. **1**, 780 (1930).

[129] Bergholm, Ann. d. Physik **53**, 169 (1917).

[130] See Mouton, Int. Crit. Tab. **7**, 112.

* Experiments on light scattering indicate that no substance is completely optically isotropic.

[131] R. de Mallemann, Ann. de Physique **2**, 1–239 (1924); **4**, 456 (1925).

small particles in suspension by an electric field are becoming of increasing interest. The first work of importance in this field was that of Cotton and Mouton,[132] who found the phenomenon in ferric hydroxide solutions. Other workers[133] have used powdered crystalline substances such as quartz, calcite, etc., in suspension in organic liquids. Recently the phenomenon has been utilized in investigations of colloids[134] and in the study of the crystallographic properties of small finely divided particles.[135] The double refraction is believed to arise from the alignment of the optically anisotropic particles by the electric field. In general, the orientation of the particles results from a difference in the dielectric properties of the small particles (crystals) in different directions, and to their shape. The influence of the shape of the particle on its orientation in the electric field is brought about by both electrical and mechanical effects. For example, if the dielectric constant of the particle is greater than that of the liquid, the particle will tend to place its longer axis along the lines of force, while a mechanical influence on its alignment can be brought about by the so-called "cataphoretic motion". Although the orientation of the particles is of course opposed by their Brownian motion, they will in some cases approach almost perfect alignment. It may be of interest to note that the size of ultramicroscopic particles could be determined by studies of the time lag of the double refraction behind the electric field.

In many instances, in addition to electric double refraction, the above mixtures or suspensions show marked dichromatism when the electric field is applied, i.e., the absorption coefficients are differentf or the components of the light vibrations parallel and perpendicular to the lines of force respectively. This phenomenon usually takes place in definite spectral regions where partial absorption occurs.

(8) The Kerr electro-optical effect in solids

The study of the Kerr effect in solids is complicated by the double refraction produced in the medium by strains arising form electrostriction and temperature gradients. In nonconducting solids the latter is negligible, but the double refraction produced by strains resulting from electrostriction is usually superimposed upon that arising from the Kerr effect. Unlike liquids, the time lag of the Kerr effect in solids is comparatively long,[2] so that the double refraction resulting from the Kerr effect is difficult definitely to separate experimentally from that produced by electrostriction, in the way Pauthenier did so successfully in liquids. However, the electrostriction can be measured experimentally or deduced theoretically and the amount of double refraction it produces determined. Tauern[136] used the following expression for computing B in glasses:

$$\frac{n_p - n_s}{\lambda} = E^2\left(B - \frac{c\epsilon}{8\pi}\right) \tag{40}$$

[132] Cotton and Mouton, Ann. Chem. Phys. **145**, 289 (1907).

[133] See Procopin, Ann. de Physique **1**, 213 (1924).

[134] Bergholm and Björnstahl, Phys. Zeits. **21**, 137 (1920).

[135] Marshall, Trans. Faraday Soc. **26**, 173 (1930).

[136] Tauern, Ann. d. Physik (4) **32**, 1064 (1910).

where c is a constant of the material obtained from separate experiments. He investigated glasses of various kinds and found that the Kerr constant increased with increasing percentages of lead in the composition of the glass. In glasses composed of almost pure silica B is very small. Other amorphous solids have been studied but not extensively.

The electric double refraction in quartz crystals was observed by Kerr[137] soon after he discovered his effect in amorphous solids. He studied the double refraction produced when the electric field was both parallel and perpendicular to the optic axes. This work has since been greatly amplified and extended by Röntgen,[138] Kundt,[139] Pockel,[140] and others.[141,142] Many different kinds of crystals have been investigated and the phenomenon found to be intimately connected with the structure and type of the crystal. A theory for the effect has been developed[140,142,143] which connects the magnitude of the phenomenon with the various constants of the crystal.

C. MAGNETIC DOUBLE REFRACTION

(1) Cotton-Mouton effect

In 1901 Kerr[144] observed that finely divided Fe_3O_4 suspended in water became doubly refracting when light traversed the medium normal to the lines of force of a magnetic field. About the same time Majoranna[145] independently discovered the phenomenon in various collodial solutions of iron. A few years later Cotton and Mouton[146] initiated an intensive study of these phenomena which resulted in their discovery of the very important effect which bears their name. They observed that many pure liquids became doubly refracting when placed in a magnetic field with the beam of light perpendicular to the lines of force,[146,147,148] i.e., an isotropic liquid when placed in a magnetic field behaved optically like a uniaxial crystal with its optic axis along the lines of force. The effect in general is comparatively small and easily confused by the larger Faraday effect (rotation of the plane of polarization of the light passing through the substance parallel to the lines of force of the magnetic field), unless special care is taken in the analysis of the emergent light. Cotton and Mouton were soon able to show that their new effect was analo-

[137] Kerr, Phil. Mag. (4) **50**, 346 (1875).

[138] Röntgen, Wied. Ann. **18**, 213 (1883).

[139] Kundt, Wied. Ann. **18**, 228 (1883).

[140] See Pockels, Lehrbuch der Kristalloptik, 492–510 Leipzig (1906).

[141] Ny Tsi Ze, C. R. **185**, 195 (1927); Jour. de Physique (6) **9**, 30 (1928).

[142] See Szivessy, Handbuch der Physik **21**, 790–802.

[143] Voigt, Wied. Ann. **69**, 297 (1899).

[144] Kerr, Brit. Assoc. Report 568 (1901).

[145] Majoranna Rendic, R. Accad. Lincei **11**, 374 (1902).

[146] Cotton and Mouton, C. R. **141**, 317, 349 (1905); **142**, 203 (1906); **145**, 229 (1907). Ann de Chem. et Phys. **11**, 145, 289 (1907).

[147] Cotton, Mouton and Weiss, C. R. **145**, 870 (1907).

[148] Cotton and Mouton, Ann. d. Chem. et Phys. **19**, 153 (1910); **28**, 209 (1913); **30**, 310 (1913); Bul. Soc. Fra. de Phys. **312**, 3 (1910); Ann. d. Chime **20**, 194 (1910); **28**, 209 (1913); Jour. de Physique **1**, 5 (1911); C. R. **147**, 193 (1908); **147**, 51 (1908); **149**, 340 (1909); **150**, 774 (1910); **150**, 857 (1910); **154**, 818 (1912); **154**, 930 (1912); **156**, 1456 (1913).

gous to the Kerr electro-optical effect and followed the same type of relations. If n_p and n_s are the indices of refraction for the components of light vibrating parallel and perpendicular to the lines of force of the magnetic field in the substance, respectively, then their phase difference D (which is a measure of the amount of double refraction) after passing a distance l through a homogeneous magnetic field H is

$$D = \frac{2\pi l(n_p - n_s)}{\lambda} = 2\pi ClH^2 \tag{41}$$

where λ is the wave-length of the light and C is the Cotton-Mouton constant. C may be either positive or negative and varies with different substances, wave-lengths, and temperatures. This law of Cotton-Mouton has been found to hold with considerable accuracy by many investigators.[149],[150]

(2) Experimental methods of study

The experimental procedures used in studying the Cotton-Mouton effect are similar to those used in investigating the Kerr electro-optical effect, except of course that the magnetic field is placed in the position of the electric field in Fig. 1. In both cases the plane polarized, monochromatic light passes through the substance normal to the lines of force (the plane of polarization of the light making 45° with the lines of force for the maximum effect), and the resulting double refraction is measured by the various standard methods previously referred to. However, more care must be taken in the case of the Cotton-Mouton effect than in the Kerr electro-optical effect because of the difficulty introduced by the almost unavoidable superimposed Faraday effect. Experimentally it is difficult to arrange the beam of polarized light so that it cuts all the lines of force exactly at right angles. Therefore, there is usually a small component of the field parallel to the light path. As a result, the rotation of the plane of polarization due to the relatively large Faraday effect must be separated from the feeble magnetic double refraction by whatever method is used for the analysis of the emergent polarized light. (It should be noted here that in the Kerr electro-optical effect this trouble does not exist, because any rotation of the plane of polarization of the light passing through a substance parallel to the electric field, i.e., the electrical analogue of the Faraday effect, is so small as to escape observation if it exists.) Method of analyzing the emergent light which separates the double refraction due to the Cotton-Mouton effect from the rotation of the plane of polarization due to the Faraday effect have been developed by numerous investigators and are described in detail in the literature.[151–156] From Eq. (41) it will be observed

[149] Skinner, Phys. Rev. 29, 541 (1909).
[150] See Szivessy, Handbuch der Physik 21, 808–823 Julius Springer (1929).
[151] Rayleigh, Phil. Mag. 4, 678 (1902).
[152] Skinner, J.O.S.A. and R.S.I. 10, 491–520 (1925).
[153] Ramanadham, Ind. Jl. Phys. 4, 12 (1929).
[154] Cotton and Dupouy, C. R. 190, 602 (1930).
[155] Cotton, C. R. 192, 1065 (1931).
[156] Dupouy and Scherer, C. R. 192, 1089 (1931).

that the magnetic field should not only be intense but at the same time as long and uniform as possible. As previously mentioned, the Cotton-Mouton effect is comparatively small in many substances so that specially designed magnets with large pole pieces are almost necessary if good results are to be obtained.[157],[158] It is probably for this reason that researches in this field have been confined to a limited number of laboratories.

(3) Theory of the Cotton-Mouton effect (Langevin-Born)

The theory of the Cotton-Mouton effect is essentially similar to that for the Kerr electro-optical effect. In fact, the two phenomena have been treated together in practically all of the theoretical work on these subjects; it being only necessary to substitute for the electrical constants, in the formulas giving the Kerr constant, the analogous magnetic constants in order to obtain values of the Cotton-Mouton constant. The Langevin-Born theory becomes applicable to the Cotton-Mouton effect if the additional assumption is made that the molecules are magnetically as well as electrically and optically anisotropic. If the molecules are magnetically anisotropic the torque exerted on the induced and on the permanent moments by the magnetic field will bring them into alignment. This alignment of the molecules is of course opposed by thermal agitation so that a condition of equilibrium is attained in which the axis of the molecule along which the largest magnetic moment exists favors the direction parallel to the magnetic field; and hence, since each molecule is optically anisotropic, the medium as a whole becomes doubly refracting. It can be shown[42],[45],[150],[159] that similarly to Eq. (16) for B for the Kerr effect the Cotton-Mouton constant C is

$$C = \frac{(n^2 - 1)(n^2 + 2)}{4n\lambda} \frac{\Theta_1 + \Theta_2}{\alpha_0}\left(1 + \frac{4}{3}\pi S_m\right)^2 \tag{42}$$

where, as before, n is the index of refraction of the medium outside the magnetic field, λ the wave-length of light, α_0 the polarizability, S_m the magnetic susceptibility and

$$\Theta_1 = \frac{1}{45kT}[(w_1 - w_2)(b_1 - b_2) + (w_2 - w_3)(b_2 - b_3) + (w_3 - w_1)(b_3 - b_1)] \tag{43}$$

$$\Theta_2 = \frac{1}{45k^2T^2}[(m_1{}^2 - m_2{}^2)(b_1 - b_2) + (m_2{}^2 - m_3{}^2)(b_2 - b_3) + (m_3{}^2 - m_1{}^2)(b_3 - b_1)] \tag{44}$$

where k is the Boltzmann constant, T is the absolute temperature b_1, b_2, b_3 as in Eq. (11) and (12) are the moments induced in a molecule along its three principal axes of optical anisotropy, or the three perpendicular axes of its optical ellipsoid, by unit electric force in the light wave acting along the three axes respectively, w_1, w_2, w_3 are the magnetic moments induced in the mole-

[157] See Cotton and Dupouy, C. R. **190**, 544, 602 (1930).
[158] Raman, Phys. Soc. Proc. **42**, 309 (1929).
[159] Debye, Marx Handbuch der Radiologie **6**, 769, Leipzig (1923).

cule by unit magnetic force acting in the same three directions respectively and m_1, m_2, m_3 are the components of the permanent magnetic moment along these same three directions. Since in many substances S_m is very small, Eq. (42) can be written

$$C = \frac{(n^2 - 1)(n^2 + 2)}{4n\lambda} \cdot \frac{\Theta_1 + \Theta_2}{\alpha_0}. \tag{45}$$

We will now consider the cases where $m = 0$ and hence from Eq. (44) $\Theta_2 = 0$. If now the value for α_0 is substituted from the Lorenz-Lorentz relation Eq. (7) into Eq. (45)

$$C = \frac{3(n^2 - 1)^2}{80\pi N n\lambda kT} \cdot \frac{(w_1 - w_2)(b_1 - b_2) + (w_2 - w_3)(b_2 - b_3) + (w_3 - w_1)(b_3 - b_1)}{(b_1 + b_2 + b_3)^2}. \tag{46}$$

To evaluate the part of the expression (46) involving w_1, w_2, w_3 and b_1, b_2, b_3, it is necessary to know the optical and magnetic constants of the molecule, along its axes of anisotropy. Information concerning the optical anisotropy is available from experiments on light scattering[61,62,63] and the Kerr electro-optical effect, but the magnetic anisotropy is best given by the Cotton-Mouton effect itself. As this magnetic anisotropy of the molecule is a very important factor in molecular structure, it may be of interest to indicate how the Cotton-Mouton constant C can be used in its evaluation. Here again, as in the case of the Kerr electro-optical effect, the Langevin-Born theory should hold strictly only in the case of gases; but the experimental data are almost completely lacking (except in the immediate region of an absorption line or band), so the computations will be confined to liquids where, at the present time, approximations only may be expected. Raman and Krishnan[49] have proposed changes in the above theory which makes it more applicable to liquids, but a discussion of this now would only complicate matters, so it will be taken up later.

Starting with the simple cases where the anisotropy of the molecule may be represented by optical and magnetic ellipsoids of revolution with their axes coincident, i.e., $b_1 = b_2$ and $w_1 = w_2$, Eq. (45) then becomes

$$C = -\frac{(n^2 - 1)(n^2 + 2)}{60n\lambda kT} \cdot \frac{b_1 - b_3}{2b_1 + b_3} [3w_3 - (w_1 + w_2 + w_3)]. \tag{47}$$

The optical anisotropy gives the expression

$$\delta = \frac{(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2}{2(b_1 + b_2 + b_3)^2} = \frac{(b_1 - b_3)^2}{(2b_1 + b_3)^2} \tag{48}$$

also

$$w_1 + w_2 + w_3 = 3\frac{S_m}{N} \tag{49}$$

where S_m is the magnetic susceptibility per unit volume. Hence

$$C = -\frac{(n^2 - 1)(n^2 + 2)}{60n\lambda kT} 3\left(w_3 - \frac{S_m}{N}\right)\delta^{1/2} \tag{50}$$

$$C = -\frac{(n^2 - 1)(n^2 + 2)}{60n\lambda kT}2(w_3 - w_1)\delta^{1/2} \tag{51}$$

or

$$\frac{w_3}{w_1} = \frac{S_m\delta^{1/2}(n^2 - 1)(n^2 + 2) - 20NC n\lambda kT}{S_m\delta^{1/2}(n^2 - 1)(n^2 + 2) + 10NC n\lambda kT}. \tag{52}$$

This last Eq. (52) makes it possible to evaluate the "magnetic anisotropy"[162] w_3/w_1 of the molecule since all the quantities on the right hand side of the equation are known or are susceptible to measurement.[160,161] In addition to w_3/w_1 the actual values of w_1 and w_3 can be obtained from Eq. (50) and (51). It should further be noted that if the values for b_1, b_2 and b_3 can be determined, for example, by means of the Kerr constant as outlines in the foregoing discussion of the Kerr electro-optical effect, from Eq. (46) and (49) the known values of the Cotton-Mouton constant C and S_m give the magnitudes of w_1 and of w_3 if we assume $w_1 = w_2$. However, if we cannot make this assumption, i.e., when w_1 w_2 w_3 each have different values, then with b_1, b_2, b_3 and S_m known Eq. (46) and (49) give the ratio between any two of the w's.

*TABLE II. *Values for the "magnetic anisotropy". w_3/w_1 computed by Ramanadham.*[162] *The values for the optical anisotropy δ were taken from a paper by Rao.*[63]

Substance	$\delta \times 10^3$ in the liquid	w_3/w_1	$C \times 10^{14}$ Liquid	Substance	$\delta \times 10^3$ in the liquid	w_3/w_1	$C \times 10^{14}$ Liquid
Saturated Hydrocarbons				*Fatty Acids*			
Pentane	3.1	0.96	−1.8	Formic acid	47.0	1.29	6.5
Heptane	2.3	0.91*	−2.5	Acetic acid	36.2	1.04	2.7
Octane	2.2	0.89	−3.0	Propionic acid	20.1	1.06	2.7
				Butyric acid	16.5	1.04	1.8
Water and saturated alcohols				*Esters of Fatty Acids*			
Water	5.53	0.81	−1.1	Ethyl formate	11.3	1.01	0.7
Methyl alcohol	3.90	0.75	−1.8				
Ethyl alcohol	2.2	0.88	−1.1	Propyl formate	5.7	1.10	2.7
Propyl alcohol	2.1	0.91	−1.1	Ethyl acetate	7.4	1.04	1.0
Butyl alcohol	2.1	0.84	−2.2	Propyl acetate	6.4	1.05	1.4
				Aromatic compounds			
Ethers				Benzene	22.5	2.10	75.0
Ethyl ether	3.2	0.88	−2.2	Toluene	21.5	1.94	67.1
Ketones				m-xylene	24.0	1.80	63.3
Acetone	8.6	1.28	4.1	p-xylene	26.0	1.80	65.3
Diethyl ketone	13.4	1.06	2.7	Chlorobenzene	26.5	1.90	81.4
				Bromobenzene	31.5	1.50	72.7
				Nitrobenzene			235.0

Table II shows some values of the magnetic anisotropy calculated by Ramanadham[162] with the method outlined above. As he points out, the values

[160] International Critical Tables, Vol. 1, 5, 6, and 7.

[161] Landolt-Börnstein Tables.

[162] Ramanadham, Ind. J. Phys. **4**, 15 (1929); **4**, 109 (1929).

* *Note added in proof*: Since the above was written Chinchalkar Ind. J. Phys. **6**, 1 (1931) has published more precise values.

in the table are probably only approximate, because the assumption, that the molecules have an axis of symmetry, used in the derivation of Eq. (52), may not be correct in every case. However, they do serve to give an idea of the order of magnitude of the magnetic anisotropy.

It will be observed from the table that the Cotton-Mouton constant C is larger in the aromatic compounds than in the aliphatic compounds. This rule is quite general and accounts for the fact that it has only been within the last few years that the magnetic double refraction has been investigated in many aliphatic substances. Also it will be noted from the table that the magnetic anisotropy is much larger in the aromatic than in the aliphatic compounds. It is strongly suggested by both the table and Eq. (52) that the feebleness of the Cotton-Mouton effect in aliphatics results from the small magnetic anisotropy rather than the small optical anisotropy of their molecules. Another interesting point that emerges from an examination of the table is that in positively doubly refracting substances $w_3 > w_1$ and in the negatively doubly refracting substances $w_3 < w_1$, i.e., as can be seen from Eq. (47) for positively doubly refracting diamagnetic substances, the direction of the axis in the molecule of maximum optical susceptibility coincides (or perhaps makes a small angle) with that of the axis of minimum magnetic susceptibility, while for negatively doubly refracting diamagnetic substances the direction of the axis of maximum optical susceptibility in the molecule is the same as that of the maximum magnetic susceptibility. Special attention should be called to the fact that saturated chain compounds have negative Cotton-Mouton constants while unsaturated compounds, containing the carbonyl group, and ring compounds, such as benzene, have positive Cotton-Mouton constants. In fact, Ramanadham has ascribed negative double refraction to the presence of saturated chemical bonds and positive double refraction to unsaturated chemical bonds. Although, as he recognizes, the data are not yet sufficient definitely to establish the rule. Scherer[163] has recently investigated the magnetic double refraction of the hydrocarbon series C_nH_{2n+2} and C_nH_n and likewise came to the conclusion that the saturated hydrocarbon chain produces an effect opposite to that of the double bond.

The table further indicates many special points of interest, such as the increase of the negative magnetic anisotropy with increase in length of the hydrocarbon chain, the tendency of the CH_3 and OH radicals to produce negative magnetic double refraction, and the comparatively large positive magnetic anisotropy of the hydrocarbon ring compounds as compared with the magnitude of the negative magnetic anisotropy of the hydrocarbon chain compounds. For example, in benzene the magnetic susceptibility of the molecule along an axis perpendicular to the ring is approximately 2.1 times that in the plane of the ring. Raman and Krishnan,[164] by assuming that the expression $[w_3 - (S_m/N)]$ in Eq. (50) is the same in benzene as in its simpler derivatives, have calculated the value of C in these derivatives. The calculated values were of the same general magnitude as the observed values but indicate

[163] Scherer, C. R. **192**, 1223 (1931).
[164] Raman and Krishnan, Proc. Roy. Soc. **A113**, 511 (1927).

that the assumption is only approximate. Nevertheless, the computations probably show that the magnetic anisotropies of these simple substituted groups are small in comparison to that of the benzene derivative as a whole.

By raising the temperature of substances which are solid at room temperature until they pass through the fusion point and become isotropic liquids, Salceanu[165] found that the magnetic double refraction was increased when the number of benzene rings in the molecules of the substance was increased[168] i.e., the Cotton-Mouton effect was greater in phenanthrene than in naphthalene which, in turn, was greater than in phenol.

(4) Theory of Raman and Krishnan for dense fluids

The more exact theory of the Cotton-Mouton effect for dense fluids given by Raman and Krishnan, like their theory for the Kerr electro-optical effect, differs from the theory previously outlined only in allowing for the anisotropy of the field on the molecule due to the surrounding molecules. It will be recalled that the Langevin-Born theory was based on the assumption that this field due to the surrounding molecules was isotropic. For this to be true, however, in the case of anisotropic molecules it is necessary for the molecules surrounding any given molecule not only to be distributed symmetrically, but in addition to have random orientations. Most substances have been shown to have anisotropic molecules from light scattering experiments while x-ray scattering experiments in liquids have demonstrated that not only the molecules are anisotropic but that the molecules immediately surrounding a given molecule are not oriented at random with respect to its principal axis, although, in the substance taken as a whole, the orientations of the molecules are random. Further failures of the quantities $(n^2-1)/(n^2+2)$ and $(\epsilon-1)/(\epsilon+2)$ to remain unchanged in passing from gases to liquid state in many cases all join in pointing to the incorrectness of the assumption of the Langevin-Born theory mentioned above. Raman and Krishnan obtain an expression analogous to Eq. (32). In general

$$C = \frac{n^2 - 1}{4\pi n\lambda} \frac{3(\Theta_1' + \Theta_2')}{\alpha_0} \tag{53}$$

$$\Theta_1' = \frac{1}{45kT}[(W_1 - W_2)(B_1 - B_2) + (W_2 - W_3)(B_2 - B_3) \\ + (W_3 - W_1)(B_3 - B_1)] \tag{54}$$

$$\Theta_2' = \frac{1}{45k^2T^2}[(M_1^2 - M_2^2)(B_1 - B_2) + (M_2^2 - M_3^2)(B_2 - B_3) \\ + (M_3^2 - M_1^2)(B_3 - B_1)] \tag{55}$$

$$
\begin{aligned}
W_1 &= w_1(1 + p_1 s_m)^2 & B_1 &= b_1(1 + q_1 s_0) \\
W_2 &= w_2(1 + p_2 s_m)^2 & B_2 &= b_2(1 + q_2 s_0) \\
W_3 &= w_3(1 + p_3 s_m)^2 & B_3 &= b_3(1 + q_3 s_0)
\end{aligned}
\tag{56}
$$

[165] Salceanu, C. R. 190, 737 (1930); 191, 486 (1930).

$$M_1 = m_1(1 + p_1 s_m) \qquad M_2 = m_2(1 + p_2 s_m) \qquad M_3 = m_3(1 + p_3 s_n.)$$

where as before s_m and s_0 are the average values for the magnetic and optical susceptibilities, $q_1 q_2 q_3$ are the electro-optical polarization factors along the three principal axes of the molecule and $p_1 p_2 p_3$ are the magnetic factors along the same directions. To evaluate C from Eq. (53) it is of course necessary to determine Θ_1' and Θ_2'. Unfortunately the experimental data are not available for this except in a few cases, and then only by means of assumptions that are not free from possible objection. In simple cases where $\Theta_2' = 0$ and where the optical and magnetic anisotropy can be represented by ellipsoids of revolution, the values of $B_1 B_2 B_3$ can be obtained from light scattering data, the indices of refraction and Kerr constants, since $q_1 q_2 q_3$ can be estimated from x-ray scattering in liquids and by calculations[166] similar to Eq. (38). Hence, it should be possible to obtain direct information concerning the W's from the value of the cotton-Mouton constant C and for the average magnetic susceptibility s_m. In general the effect of the modifications in the Langevin-Born theory introduced by Raman and Krishnan tends to reduce the magnetic double refraction to be expected. The modified expressions of Raman and Krishnan are in better agreement with experiments than the older theory, but they introduce quantities that are very difficult to evaluate with precision without the aid of uncertain assumptions.

Cotton-Mouton constant of substances in solution

Experiments on the magnetic properties of crystals[167] show that the magnetic susceptibility of some crystals is not the same in different directions. This magnetic anisotropy of crystals is often quite marked and exists in both organic and inorganic compounds. Generally these magnetically anisotropic crystals also show optical anisotropy as is evidenced by the existance of double refraction. Ramanadham[168] has attempted to correlate these anisotropic optical and magnetic properties of crystals with the Cotton-Mouton constants found by desolving the crystalline substance in a solvent which possesses a negligible or very small magnetic double refraction. By this procedure he found in some cases, especially in certain aromatic substances, that the value of the Cotton-Mouton effect of the solution was of the same order of magnitude as was calculated on the supposition that the magnetic and optical properties of the crystal were ascribable to the magnetic and optical properties of the molecules of which it was composed. However, as he pointed out, in order to make a direct connection between the anisotropy of the crystal and the anisotropy of the molecules or ions composing the crystal, it is necessary to know the way in which the molecules or ions are oriented relatively to each other, their orientation with respect to the geometrical axes of the crystal, the number in each unit cell and their spacing. On the other hand, if the value of the Cotton-Mouton constant is known, obviously it can be used as a valuable auxiliary to the x-ray analysis of crystal structure. Indeed it has

[166] See Krishnan and Rao, Ind. J. Phys. **4**, 39 (1929).

[167] See Bhagavantam, Ind. J. Phys. **4**, 1 (1929).

[168] Ramanadham, Ind. J. Phys. **4**, 109 (1929).

been emphasized by Professor Raman[168] that, taken together with the investigations of the anisotropy of the magnetic and optical characteristics of crystals, the Cotton-Mouton effect of the crystalline compounds in solution can reveal properties and structure of the crystal not at present possible of determination by x-ray analysis. It should not be overlooked however, that either the anisotropic optical and magnetic properties of the molecule must remain unchanged, or else change in a known way during the change of state of the substance if the information concerning the properties and structure of crystals obtained from the Cotton-Mouton constant, as mentioned above, is to be depended upon to be quantitatively correct. Nevertheless, in many cases qualitative information is of great value in supplementing the x-ray analysis, as has been demonstrated recently by workers in Professor Raman's laboratory.[167]

The study of the magnetic double refraction of substances in solution, besides aiding in crystal analysis, has also revealed many interesting facts concerning molecular structure and the liquid state. For example, the Cotton-Mouton constant for nitric acid has been used together with the light-scattering coefficient r to compute the magnetic anisotropy of the NO_3 ion.[169] With this information it is possible to obtain directly the magnetic effect of, say, the alkaline ion in the alkaline nitrates, since the Cotton-Mouton constants of these have been measured in solution.[168] Incidentally it was found that the nitrates have a smaller positive magnetic double refraction than the nitrites, which supports the previous conclusion that chemical unsaturation tends to produce increased positive magnetic double refraction. The effect of the state of the substance* on the Cotton-Mouton constant is well illustrated by the remarkable decrease in the specific magnetic double refraction in nitro compounds in dilute solution.[170,171,172,168] It will be recalled in connection with this that the specific optical anisotropy also shows a decrease in nitrobenzene in going from pure liquid to vapor. In most "normal" liquids, however, the opposite is observed.

(5) The variation of C with wave-length of the light and temperature

Cotton and Mouton[173] in their early work found that in nitrobenzene the variation of the magnetic double refraction with the wave-length of the light passing through the substance was similar to the variation of the electric double refraction with wave-length. Skinner,[149] in extending this work, found that the ratio of the Cotton-Mouton constant C, taken from his measurements, to the Kerr constant B as measured by McComb, was approxi-

[169] Krishnan and Raman, Proc. Roy. Soc. A115, 550 (1927).

[170] Cotton and Mouton, C. R. 156, 1456 (1913); Ann. de Chemie et Phys. 28, 209 (1913).

[171] Szivessy, Zeits. f. Physik 7, 285 (1921).

[172] Szivessy and Richartz, Ann. d. Physik 86, 393 (1928).

* The average magnetic susceptibility s_m has been found by Oxley, Phil. Trans. 214, 109 (1914); 215, 79 (1915); 220, 247 (1928) to change as the substance passes from the crystalline state to the liquid state.

[173] Cotton and Mouton, C. R. 147, 193 (1908); 150, 857 (1910); Jour. de Physique 5, 1, 5 (1911); Ann. de Chemie et Physique 8, 20, 213 (1910).

mately independent of the wave-length of the light used. He also found that the dispersion in the magnetic double refraction followed Havelock's law

$$C = h \frac{(n^2 - 1)^2}{n\lambda} \tag{57}$$

which is analogous to Eq. (5) and Eq. (26) for the dispersion of the electric double refraction. It will be observed that Eq. (47) reduces directly to Eq. (57) if the optical and magnetic anisotropies of the molecules do not change with wave-length. Subsequent workers have generally verified Havelock's laws, although there are indications of slight variations. It would be of special interest in view of the recent work by Szivessy and his co-workers[174] on the dispersion of the electric double refraction in the ultraviolet and that by Ingersoll in the infrared, to obtain data on the magnetic double refraction in these regions.

The variation of the Cotton-Mouton[175] constant with temperature, wavelength being constant, has been studied in several liquids,[176,177] especially by Szivessy. His results are in rough accord with the theory of Langevin, although in some cases he noted marked discrepancies. Langevin's formula is easily derived from Eq. (45) by substituting for α_0 from Eq. (46) and assuming $\Theta_2 = 0$. Then

$$C = K \frac{\rho(n^2 + 2)^2}{n\lambda T} \tag{58}$$

where ρ is the density and K is a constant assumed independent of the temperature. This latter assumption is perhaps not justified, for it would mean that the effective optical and magnetic anisotropies of the molecule were independent of the temperature or else, as is improbable, varied in such a way as to counterbalance each other in Eq. (58). The effective optical anisotropy of the molecules of several liquids have been found to change with temperature. Most "normal" liquids showed an increase of optical anisotropy with increase of temperature, but in some liquids that are supposed to be "associated," the opposite is observed over certain temperature ranges. An increase of anisotropy with increase of temperature is in accord with the theory of Raman and Krishnan. It would be of interest to have more careful measurements of C as a function of temperature, since, with the changes in the optical anisotropy as a function of temperature known, the changes in the magnetic anisotropy as a function of temperature might be traced.

(6) Magnetic double refraction in gases

Magnetic double refraction in gases and vapors was predicted by Voigt[178]

[174] Szivessy, Ann. d. Physik **69**, 237 (1922); Zeits. f. Physik **18**, 97 (1923); Handbuch der Physik 880–882.

[175] Mouton, Int. Crit. Tab. **7**, 109–113.

[176] Cotton and Mouton C. R. **149**, 340 (1909).

[177] Szivessy, Ann. d. Physik **68**, 127 (1922); **69**, 231 (1922). See Handbuch der Physik **21**, 882–883, Leipzig (1929).

[178] Voigt, Wied. Ann. **67**, 360 (1899); Electro and Magneto Optics. See "Magneto-optik" Gaetz Handbuch der Elekt. und Mag., Leipzig (1915), 4 (1920).

from his theory of magneto-optics. Later he succeeded in observing the phenomenon for the first time in sodium vapor in the spectral region near the D lines. Following this work Zeeman[179] and others showed that Voigt's theory was quantitatively verified in the immediate vicinity of the absorption lines, where anomalous dispersion occurs. It is now generally believed that this magnetic double refraction near an absorption line has a direct relation to the Zeeman effect.[180,181]

The magnetic double refraction of gases and vapors in spectral regions not close to their characteristic absorption lines is very feeble if it exists. The Stern-Gerlach[182] experiment and the theory[183,184] of the "quantizing of direction in a magnetic field" have indicated that the atoms of a paramagnetic gas under the proper conditions of temperature and pressure should be aligned by the magnetic field. If then the atoms are optically anisotropic, magnetic double refraction should be observable for wave-lengths far removed from an absorption line where there are no anomalous values for the index of refraction. The amount of the double refraction would be almost independent of the strength of the magnetic field when the latter exceeded a comparatively small value. Experiments[185,186,187] made with the view of testing this hypothesis have indicated that, in sodium vapor, potassium vapor, oxygen and nitric oxide, the magnetic double refraction in the spectral regions tested was too small to observe, although an easily measurable amount should have existed. Krishnan[187] has concluded from his experiments that paramagnetic molecules and atoms do not align themselves, at least as a whole, in a magnetic field in the way postulated above. He suggests a possible escape from this conclusion by assuming that there exists in each case an angle of just the proper magnitude between the axis of the optical ellipsoid of the molecule or atom and the direction of its permanent paramagnetic moment. If this were the case, alignment could take place without appreciable resulting double refraction. However, he regards this as highly improbable. He further cites the negative results of Debye and Huber as supporting his conclusion. These experimenters[188,189] were unable to find an electrical potential induced across two metallic plates when placed in a polar paramagnetic gas transversely to a magnetic field. If the polar molecules were oriented by the magnetic field according to the above hypothesis, a measurable electric potential should have been noted unless the electric moment of the molecule was almost perpendicular to its magnetic moment. It is indeed unfortunate that the appa-

[179] Zeeman and Geest, Proc. Amsterdam Acad. 435 (1904).
[180] Zeeman, Researches in Magneto-optics 85, McMillan Co. (1913).
[181] Wood, Physical Optics 544 (1923).
[182] Stern, Zeits. f. Physik 7, 249 (1921).
[183] Gerlach and Stern, Zeits. f. Physik 8, 10 (1921); 9, 349 (1922).
[184] Sommerfeld, Wave Mechanics 96–98 E. P. Dutton and Co. (1929).
[185] Schutz, Zeits. f. Physik 38, 853 (1926).
[186] Fraser, Phil. Mag. 1, 885 (1926).
[187] Krishnan, Ind. J. Phys. 1, 245 (1926–27); 1, 33 (1926).
[188] Debye, Zeits. f. Physik 36, 300 (1926).
[189] Huber, Phys. Zeits. 27, 619 (1926).

ratus at present available does not seem to be sensitive enough to measure magnetic double refraction in gases except near absorption lines or bands, for in the gaseous state the unknown influence of the surrounding molecules becomes either negligible or isotropic, and the Langevin-Born theory should apply strictly.

(7) Miscellaneous

Attention should again be called to an effect mentioned at the beginning of the discussion of the Cotton-Mouton effect. If some finely divided substances suspended in liquids are subjected to a magnetic field, they give a large magnetic double refraction when the light passes normal to the lines of force.[144,145,146] "Fer Bravais" and many iron colloids show a very large magnetic double refraction while, in some of the so called "crystalline" liquids, the magnitude of the effect is over a million times as great as the Cotton-Mouton effect in "normal" liquids. The experiments indicate that the particles of the above substances are both optically and magnetically anistropic and hence are oriented by the magnetic field and produce double refraction. In the case of "crystalline" liquids and some colloids the particles seem to be almost completely aligned by comparatively weak magnetic fields. However, the phenomena in some cases are rather complicated, as is shown by certain changes with time and the peculiar variations observed with different wave-lengths. Even dichromatism is often present. In many cases, times of the order of magnitude of seconds are required for the full effect to take place after the application of the magnetic field, which indicates that the particles are actually being aligned by the field. The magnetic double refraction in optically active liquids has also been studied both experimentally and theoretically somewhat in detail by de Mallemann.[192]

(8) Magnetic double refraction in solids

The magnetic double refraction of pure amorphous substances in the solid state has not been extensively investigated. Such studies are always complicated by double refraction set up by strains resulting from magnetostriction for, unlike the Faraday effect, the phenomenon is rather feeble. On the other hand, the effects produced by crystals on light passing normal to the lines of force have been studied somewhat in detail. Becquerel[193,194,195] and his associates have made very interesting studies of the magneto-optical effects produced in crystals of the rare earths. These crystals show narrow absorption lines at low temperatures, and Becquerel[196] has confined his studies principally to the effect at these lines or in their immediate spectral regions when

[190] Dressellhorst, Freundlich and Leonardt, Elster-Geitel-Festschrift, 476 (1915).
[191] Björnstahl, Phil. Mag. **42,** 352 (1921).
[192] R. de Mallemann, C. R. **176,** 380 (1923); Ann. d. Physik **2,** 523 (1924).
[193] See Szivessy, Handbuch der Physik **21,** 823, Julius Springer (1929).
[194] J. Becquerel, Le radium **4,** 49 (1907); **5,** 5 (1908); **6,** 327 (1909); Comm. Leiden **18,** no. 68a (1929).
[195] Kramers and Becquerel, Comm. Leiden **18,** no. 68c (1929).
[196] Becquerel and Matout, C. R. **192,** 1091 (1931).

the magnetic field is oriented in various directions with respect to the optic axis of the crystal. The phenomena observed are rather complicated and it is necessary to refer to the original work for detailed information. However, he has shown that the effects which he observed are probably of the same nature as the Zeeman effect.

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