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Section A.—Mathematical and Physical Sciences.

A Theory of Electric and Magnetic Birefringence in Liquids. By Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN.

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1. Introduction.

The double refraction exhibited by liquids when placed in an electrostatic field is ascribed in the theory of Langevin* to an orientation of the molecules produced by the field, the orientative couple arising from an assumed electrical anisotropy of the molecule. If an optical anisotropy of the molecule is postulated in addition, the birefringence of the liquid follows as a necessary consequence. Born't modified the Langevin theory by including also the orientative effect of the field on the molecule due to the permanent electric moment, if any, possessed by it. The optical anisotropy and electrical polarity of the molecule postulated in these theories can be independently determined from observations of light-scattering and dielectric constant in the vapours of the substances. In two recent papers[±] we have attempted to discuss how far the available data for the Kerr effect can be reconciled with the theories of Langevin and Born. The main result emerging is that these theories fail to give the magnitude of the Kerr constant in *liquids* correctly in terms of the constants of the molecule as determined in the gaseous condition. This failure is illustrated in Table I for a number of liquids having non-polar molecules for which the optical anisotropy is known from observations on light-scattering in the vapour.

It appears hardly likely that the failure of the Langevin theory indicated by the figures in Table I can be ascribed to a real change in the optical anisotropy of the molecule when it passes from the condition of vapour to that of liquid. It seems rather that the explanation must lie in the inadequacy of the theory itself. We accordingly propose in this paper to put forward a theory of electric and magnetic double refraction, in which the fundamental premises of Langevin and Born are revised.

* 'Le Radium,' vol. 9, p. 249 (1910).

† 'Ann. der Physik,' vol. 55, p. 177 (1918).

‡ 'Phil. Mag.,' vol. 3, pp. 713 and 724 (1927).

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	Depolarisation of the light scattered by the corre- sponding vapour.	Kerr constant \times 10 ⁹ .	
Liquid.		Calculated accord- ing to Langevin's theory.	Observed.
	Per cent.		·····
Pentane	1.28	17.9	5.0
Isopentane	1.2	$16 \cdot 2$	$5 \cdot 0$
Herano	1.41	19.7	$\left\{ \begin{array}{c} 4\cdot 5\\ 5\cdot 6\end{array} \right.$
Heptane	1.40	30	$\left\{ \begin{array}{c} 7\cdot 1 \\ 10\cdot 5 \end{array} \right.$
Octane	1.66	43	$\left\{ \begin{array}{c} 7 \cdot 7 \\ 13 \cdot 6 \end{array} \right\}$
Carbon tetrachloride	0.6	14.4	7.4
Carbon bisulphide	10.7	390	$322 \cdot 6$
Benzene		122	59.3
Cyclohexane	1.26	26	7.4

Ta	ble	I.

2. The Polarisation Field in Liquids.

Both Langevin and Born assume that, while the molecule individually is anisotropic, the polarisable matter present round it is so distributed that the local polarisation field acting on the molecule is independent of its orientation in the field. There is reason to believe that this assumption cannot be correct in a dense fluid, and that, in addition to considering the anisotropy of the molecule itself, we have also to postulate an anisotropic distribution of polarisable matter in its immediate neighbourhood. For the purpose of a purely formal mathematical theory it is unnecessary to discuss in detail how such anisotropic distribution of matter arises. We assume only that the orientation of the molecule determines the distribution of matter around it, and therefore also the local polarisation field acting on it. That the polarisation field acting on a molecule may vary with its orientation in the liquid has been previously suggested by other writers, notably Havelock* and Lundblad.† But while these writers have put forward the hypothesis as an independent theory of electric double refraction, we, on the other hand, consider it only as modifying the premises of the Langevin-Born theory, and find that its effect, in general, is actually to diminish the magnitude of the Kerr effect to be expected. Independent evidence in support of the hypothesis is furnished by studies of X-ray diffraction, by the deviations from the Lorentz refraction formula, and by observations of light-scattering, in liquids. In order, however, not unduly to lengthen this paper, we refrain from presenting this evidence here, and will merely assume the existence of the "anisotropic" polarisation field.

* 'Roy. Soc. Proc.,' A, vol. 84, p. 492 (1911).

† 'Optik der dispergierenden Medien,' p. 57 (Upsala, 1920).

The total polarisation field in a liquid is usually put equal to $\frac{4}{3}\pi\chi E$, where E is the acting external field, static or optic, as the case may be, and χ is the corresponding susceptibility of the fluid per unit volume. (In what follows the susceptibility in the electrostatic and optical cases will be denoted by χ_e and χ_0 respectively.) We modify the foregoing assumption and consider the local polarisation field acting on a molecule to be dependent on its orientation with respect to the external field. Let us assume that, when an external electrostatic field E is incident in succession along the three principal electrostatic axes of the molecule, the polarisation field acting on it, due to the surrounding molecules, is also in the same direction, being equal to $p_1\chi_e E$, $p_2\chi_e E$, and $p_{3\chi_e}E$, respectively. Similarly, when an optical field E is incident in succession along the three optic axes of the molecule, let the optical polarisation field acting on it lie in the same direction and be equal to $q_1\chi_0 E$, $q_2\chi_0 E$, and $q_{3\chi_0}$ E, respectively. It is possible to discuss the general case when the electrical and the optic axes of the molecule have different directions. However, the expressions come out simpler when the two sets of axes are taken to be coincident, and since we have reason to believe from independent considerations that this assumption cannot be far from the truth, we confine ourselves to this simple case.

3. Molecular Orientation in the Field.

We proceed to derive an expression for the potential energy of the molecules when placed in an electro- or magneto-static field. Since the discussion will be exactly similar for the two cases, we shall, in what follows, treat specifically only the electrical case.

Let a_1 , a_2 , a_3 be the moments induced in a molecule by unit electrostatic field *actually* acting on it, respectively along its three axes, and let b_1 , b_2 , b_3 be the corresponding moments induced by unit field of a light-wave; μ_1 , μ_2 , μ_3 are the components along these axes of the permanent electric moment of the molecule.

Suppose now an electrostatic field E is incident along the z-axis of a system of co-ordinates fixed in space. Then the actual fields acting along the axes of any molecule are $E\alpha_1 (1 + p_1\chi_e)$, $E\alpha_2 (1 + p_2\chi_e)$, and $E\alpha_3 (1 + p_3\chi_e)$, respectively, where $\alpha_1, \alpha_2, \alpha_3$ are the direction-cosines of these axes with respect to the direction of E. Denoting the orientation of the axes of the molecule with respect to the co-ordinate axes fixed in space by the usual Eulerian angles θ, ϕ, ψ , we have

$$\begin{array}{c} \alpha_{1} = -\sin\theta\cos\psi\\ \alpha_{2} = \sin\theta\sin\psi\\ \alpha_{3} = \cos\theta \end{array} \right\}$$
 (1)

The potential energy of the molecule in the field is given by

$$u = -\left[\mu_1(1+p_1\chi_e)\alpha_1 + \mu_2(1+p_2\chi_e)\alpha_2 + \mu_3(1+p_3\chi_e)\alpha_3\right] \mathbf{E} - \frac{1}{2}\left[a_1(1+p_1\chi_e)^2\alpha_1^2 + a_2(1+p_2\chi_e)^2\alpha_2^2 + a_3(1+p_3\chi_e)^2\alpha_3^2\right] \mathbf{E}^2, \quad (2)$$

which may, for brevity, be denoted by

$$-(M_{1}\alpha_{1} + M_{2}\alpha_{2} + M_{3}\alpha_{3}) E - \frac{1}{2}(A_{1}\alpha_{1}^{2} + A_{2}\alpha_{2}^{2} + A_{3}\alpha_{3}^{2}) E^{2}, \qquad (3)$$

where

$$\begin{array}{l} \mathbf{M}_{1} = \mu_{1} \left(1 + p_{1} \chi_{e} \right) \\ \mathbf{M}_{2} = \mu_{2} \left(1 + p_{2} \chi_{e} \right) \\ \mathbf{M}_{3} = \mu_{3} \left(1 + p_{3} \chi_{e} \right) \end{array} \right\}$$

$$(4)$$

and

$$\begin{array}{c} \mathbf{A}_{1} = a_{1} \left(1 + p_{1} \chi_{e} \right)^{2} \\ \mathbf{A}_{2} = a_{2} \left(1 + p_{2} \chi_{e} \right)^{2} \\ \mathbf{A}_{3} = a_{3} \left(1 + p_{3} \chi_{e} \right)^{2} \end{array} \right\} .$$
 (5)

Since u is a function of the direction cosines of the axes of the molecule, there will be a tendency for the molecules in the medium to orientate, thermal agitation, of course, acting against it. When equilibrium is established, from Boltzmann's theorem, the number of molecules per unit volume, the directions of whose axes are determined by the range sin $\theta \ d\theta \ d\phi \ d\psi$, is equal to

$$Ce^{-\frac{u}{kT}}\sin\theta\,d\theta\,d\phi\,d\psi,\tag{6}$$

where C is a constant given by the relation

 $\nu =$ total number of molecules per unit volume

$$= C \int e^{-\frac{u}{kT}} \sin \theta \, d\theta \, d\phi \, d\psi.$$
⁽⁷⁾

4. Calculation of Birefringence.

We have now to find the effect of this orientation on the refractive index of the medium for light-vibrations parallel and perpendicular to the electrostatic field.

Case I.—Let the electric vector of the incident light-wave (= Z, say) be assumed to lie along the z-axis, *i.e.*, along the electrostatic field. The actual optical moments induced in a molecule along its axes are $b_1 (1 + q_1 \chi_{02}) \alpha_1 Z$, $b_2 (1 + q_2 \chi_{02}) \alpha_2 Z$, $b_3 (1 + q_3 \chi_{02}) \alpha_3 Z$, χ_{02} being the optical susceptibility along the z-axis of the medium per unit volume. For brevity we may denote these expressions by $B_{1z}\alpha_1 Z$, $B_{2z}\alpha_2 Z$, and $B_{3z}\alpha_3 Z$, respectively.

These moments, when resolved along the z-axis, are together equal to

$$(B_{1z}\alpha_1^2 + B_{2z}\alpha_2^2 + B_{3z}\alpha_3^2)Z$$
(8)

 $= m_z Z$, say.

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The average value of m_z taken over all the molecules is given by

$$\overline{m_z} = \frac{\int e^{-\frac{w}{kT}} m_z \sin \theta \, d\theta \, d\phi \, d\psi}{\int e^{-\frac{w}{kT}} \sin \theta \, d\theta \, d\phi \, d\psi}, \qquad (9)$$

which, after a long calculation, reduces to

$$\overline{m_z} = \frac{B_{1z} + B_{2z} + B_{3z}}{3} + 2 \left(\Theta_{1z} + \Theta_{2z}\right) \frac{E^2}{2},$$
(10)

where

$$\Theta_{1z} = \frac{1}{45kT} \left[(A_1 - A_2) (B_{1z} - B_{2z}) + (A_2 - A_3) (B_{2z} - B_{3z}) + (A_3 - A_1) (B_{3z} - B_{1z}) \right]$$
(11)

$$\Theta_{2z} = \frac{1}{45k^2 T^2} [(M_1^2 - M_2^2) (B_{1z} - B_{2z}) + (M_2^2 - M_3^2) (B_{2z} - B_{3z}) + (M_2^2 - M_3^2) (B_{z} - B_{zz})]$$
(12)

Also

$$\chi_{0z} = \sqrt{m_z}.$$
 (13)

Case II.—The light-vector is perpendicular to the electrostatic field, say, along the x-axis.

We can show, just as in Case I, that the average contribution from a molecule to the optical moment along the x-axis is given by

$$\overline{m_x} = \frac{B_{1x} + B_{2x} + B_{3x}}{3} - (\Theta_{1x} + \Theta_{2x}) \frac{E^2}{2}, \qquad (14)$$

where

$$B_{1x} = b_1 (1 + q_1 \chi_{0x}) B_{2x} = b_2 (1 + q_2 \chi_{0x}) B_{3x} = b_3 (1 + q_3 \chi_{0x})$$
(15)

 χ_{0x} being the optical susceptibility of the medium along the x-axis.

$$\chi_{0x} = \sqrt{m_x}.$$
 (16)

$$\Theta_{1x} = \frac{1}{45kT} [(A_1 - A_2) (B_{1x} - B_{2x}) + (A_2 - A_3) (B_{2x} - B_{3x}) + (A_3 - A_1) (B_{3x} - B_{1x})].$$
(17)

$$\Theta_{2x} = \frac{1}{45k^2 T^2} \left[(M_1^2 - M_2^2) (B_{1x} - B_{2x}) + (M_2^2 - M_3^2) (B_{2x} - B_{3x}) + (M_3^2 - M_1^2) (B_{3x} - B_{1x}) \right].$$
(18)

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From equations (10) and (14)

$$\overline{m_{z}} - \overline{m_{x}} = \frac{1}{3} \left(b_{1}q_{1} + b_{2}q_{2} + b_{3}q_{3} \right) \left(\chi_{0z} - \chi_{0z} \right) \\ + \left[2 \left(\Theta_{1z} + \Theta_{2z} \right) + \left(\Theta_{1x} + \Theta_{2x} \right) \right] \frac{E^{2}}{2}.$$
(19)

If n_p and n_s are the refractive indices of the medium for vibrations along and perpendicular to the field,

$$\overline{m_{z}} = \frac{n_{p}^{2} - 1}{4\pi\nu}; \quad \overline{m_{x}} = \frac{n_{s}^{2} - 1}{4\pi\nu},$$

$$\overline{m_{z}} - \overline{m_{x}} = \frac{n_{p}^{2} - n_{s}^{2}}{4\pi\nu} = \frac{n_{0} (n_{p} - n_{s})}{2\pi\nu},$$
(20)

 n_0 being the mean refractive index of the medium.

Also

$$\chi_{0z} - \chi_{0x} = \nu \left(\overline{m_z} - \overline{m_x} \right). \tag{21}$$

From (20), (21) and (19) we have

$$n_{p} - n_{s} = \frac{2\pi\nu}{n_{0}} \cdot \frac{2\left(\Theta_{1z} + \Theta_{2z}\right) + \left(\Theta_{1x} + \Theta_{2x}\right)}{1 - \frac{\nu}{3}(b_{1}q_{1} + b_{2}q_{2} + b_{3}q_{3})} \cdot \frac{E^{2}}{2}.$$
 (22)

Since the values of the optical susceptibility of the medium along and perpendicular to the field are nearly equal, we may write in equation (22)

$$egin{aligned} \Theta_{1z} &= \Theta_{1x} = \Theta_1 \ \Theta_{2z} &= \Theta_{2x} = \Theta_2 \end{aligned}$$

where

and

$$\Theta_{1} = \frac{1}{45kT} \left[(A_{1} - A_{2}) (B_{1} - B_{2}) + (A_{2} - A_{3}) (B_{2} - B_{3}) + (A_{3} - A_{1}) (B_{3} - B_{1}) \right], \quad (23)$$

$$\Theta_{2} = \frac{1}{45k^{2}T^{2}} \left[(M_{1}^{2} - M_{2}^{2}) (B_{1} - B_{2}) + (M_{2}^{2} - M_{3}^{2}) (B_{2} - B_{3}) + (M_{3}^{2} - M_{1}^{2}) (B_{3} - B_{1}) \right], \quad (24)$$

$$B_{1} = b_{1} (1 + q_{1}\chi_{0})
B_{2} = b_{2} (1 + q_{2}\chi_{0})
B_{3} = b_{3} (1 + q_{3}\chi_{0})$$
(25)

 χ_0 being the mean value of the optical susceptibility of the medium.

б

Also

$$\chi_{0} = \nu \frac{b_{1}(1 + q_{1}\chi_{0}) + b_{2}(1 + q_{2}\chi_{0}) + b_{3}(1 + q_{3}\chi_{0})}{3}$$

$$= \frac{\nu \gamma_{0}}{1 - \frac{\nu}{3}(b_{1}q_{1} + b_{2}q_{2} + b_{3}q_{3})},$$
(26)

where

$$\gamma_0 = \frac{b_1 + b_2 + b_3}{3}.$$

Substituting in (22), we finally obtain for the Kerr constant

$$\mathbf{K} = \frac{n_p - n_s}{\lambda \mathbf{E}^2} = \frac{n_0^2 - 1}{4n_0\lambda} \cdot \frac{3 (\Theta_1 + \Theta_2)}{\gamma_0}.$$
 (27)

When the polarisation field acting on the molecules is isotropic,

$$p_1 = p_2 = p_3 = \frac{4\pi}{3},$$

and also

$$q_1 = q_2 = q_3 = \frac{4\pi}{3};$$

$$\Theta_{1} = \frac{1}{45kT} \left[(a_{1} - a_{2}) (b_{1} - b_{2}) + (a_{2} - a_{3}) (b_{2} - b_{3}) + (a_{3} - a_{1}) (b_{3} - b_{1}) \right] \left(\frac{\delta + 2}{3} \right)^{2} \cdot \frac{n_{0}^{2} + 2}{3}$$
(28)

and

$$\begin{split} \Theta_{2} &= \frac{1}{45k^{2}\mathrm{T}^{2}} \left[(\mu_{1}^{2} - \mu_{2}^{2}) (b_{1} - b_{2}) + (\mu_{2}^{2} - \mu_{3}^{2}) (b_{2} - b_{3}) \right. \\ &+ (\mu_{3}^{2} - \mu_{1}^{2}) (b_{3} - b_{1}) \left[\left(\frac{\delta + 2}{3} \right)^{2} \cdot \frac{n^{2} + 2}{3}, \quad (29) \end{split}$$

where δ is the dielectric constant of the medium; and expression (27) naturally reduces to that given by the Langevin-Born theory.*

In the above discussion we have entirely neglected the effect of electrostriction, since it will not affect the value of the *difference* in refractive indices for vibrations along and perpendicular to the incident field.

5. Comparison of Theory and Observation.

In order to apply the foregoing modified formula to any actual liquid, we have to make some assumptions regarding the origin of the anisotropy of the polarisation field. The anisotropy might arise in the following way. We replace for simplicity the molecules in the medium by the equivalent doublets

* See Debye, Marx's 'Handbuch der Radiologie,' vol. 6, p. 768.

placed at their respective centres. The finite size of the molecules imposes naturally a limit to the closeness of approach of the doublets towards each other. Round any particular molecule as centre we can describe a closed surface, entry into which by other molecules is excluded by reason of their finite size. The form of the surface will naturally be determined by the shape of the molecule and will therefore, in general, be non-spherical, *i.e.*, the distribution of polarisable matter around the molecule under consideration will have no spherical symmetry with respect to it, and hence arises an anisotropy in the polarisation field.

We may provisionally represent this surface by an ellipsoid having the molecule at its centre, and consider, as an approximation, the distribution as well as the orientation of the molecules outside to be entirely fortuitous. Then the polarisation field at the centre of the ellipsoid will be equivalent to that due to a surface charge $-\chi E \cos \theta$ per unit area at any point of the surface of the ellipsoid the normal to which makes an angle θ with the direction of E.

Let us consider two simple cases.

Case I.—The ellipsoid is a prolate spheroid of revolution ;

$$b=c=\sqrt{1-e^2}$$
. a ,

say, where a, b, c are the semi-axes of the ellipsoid. The polarisation constants along the axes are*

$$p_1 = 4\pi \left(\frac{1}{e^2} - 1\right) \left(\frac{1}{2e} \log \frac{1+e}{1-e} - 1\right)$$
(30)

$$p_2 = p_3 = 2\pi \Big(\frac{1}{e^2} - \frac{1 - e^2}{2e^3} \log \frac{1 + e}{1 - e} \Big). \tag{31}$$

As an example we may take pentane, which is a fairly elongated molecule. From X-ray measurements the cross-sectional diameter of the molecule is equal to 4.90 Å.U. and its length is about 8.7 Å.U. Hence, as an approximation, we may take for the semi-axes of the ellipsoid

$$a = \left(\frac{8 \cdot 7}{2} + \frac{4 \cdot 9}{2}\right) \text{ Å.U.} = 6 \cdot 8 \text{ Å.U.},$$
$$b = c = 4 \cdot 9 \text{ Å.U.}$$

On calculation from these dimensions

$$p_1 = q_1 = 3 \cdot 15,$$

$$p_2 = p_3 = q_2 = q_3 = 4 \cdot 71.$$

* See Maxwell, 'Treatise on Electricity and Magnetism,' 3rd edn., vol. 2, p. 69.

We may also reasonably take the optical ellipsoid of the molecule to be a prolate spheroid of revolution about the geometrical axis of the molecule. Using for the depolarisation factor of the light scattered by the vapour the value r = 0.0128 and for the refractivity at 0°C., $n - 1 = 1.711 \times 10^{-3}$ per atm.,

	$b_1 = 12 \cdot 15 \times 10^{-24},$
Hence	$b_2 = b_3 = 9 \cdot 01 \times 10^{-24}.$
	$A_1 = 17 \cdot 88 \times 10^{-24}$,
Also	${f A_2}{=}{f A_3}{=}15{\cdot}66 imes10^{-24}$.
AISO	$B_1 = 14.74 \times 10^{-24}$,
ጠ ና	$B_2 = B_3 = 11.88 \times 10^{-24}.$
Therefore	$\mathrm{K}=5{\cdot}5 imes10^{-9}$,

as against 17.9×10^{-9} calculated according to the Langevin theory.

The observed value = $5 \cdot 0 \times 10^{-9}$.

Case II.—The ellipsoid surrounding the molecule is an oblate spheroid of revolution:

 $a = b = \frac{c}{\sqrt{1 - e^2}}.$

Then

$$p_1 = p_2 = 2\pi \left(\frac{\sqrt{1 - e^2}}{e^3} \sin^{-1} e - \frac{1 - e^2}{e^2} \right), \tag{32}$$

$$p_3 = 4\pi \Big(\frac{1}{e^2} - \frac{\sqrt{1-e^2}}{e^3} \sin^{-1} e \Big).$$
 (33)

As an example for this case we may take benzene. The X-ray diffraction pattern of the liquid has been critically studied by Prof. Sogani^{*} and shows two rings corresponding to mean molecular distances of 4.90 Å.U. and about 3.42 Å.U. respectively. Solid benzene also gives very intense lines, corresponding to a spacing approximately equal to the above distances.[†] We may reasonably take these distances for the semi-axes of the ellipsoid

$$a = b = 4.90$$
 Å.U.,
 $c = 3.42$ Å.U.

We then obtain

$$p_1 = p_2 = q_1 = q_2 = 3 \cdot 56 ;$$

$$p_3 = q_3 = 5 \cdot 44.$$

* 'Indian Journal of Physics,' vol. 1, p. 357 (1927).

† Broomé, 'Phys. Z.,' vol. 24, p. 124 (1923).

From r = 0.0440 for the vapour and from the refractivity, assuming the optical ellipsoid of the molecule to be an oblate spheroid of revolution about the geometric axis, we get

$$\begin{split} b_1 &= b_2 = 12 \cdot 33 \times 10^{-24}, \\ b_3 &= 6 \cdot 26 \times 10^{-24}, \\ A_1 &= A_2 = 22 \cdot 36 \times 10^{-24}, \\ A_3 &= 14 \cdot 63 \times 10^{-24}, \\ B_1 &= B_2 = 16 \cdot 61 \times 10^{-24}, \\ B_3 &= 9 \cdot 57 \times 10^{-24}, \\ K &= 6 \cdot 2 \times 10^{-8}, \end{split}$$

Also

Hence

as against the value $12\cdot 2\times 10^{-8}$ calculated according to Langevin's theory.

The observed value = $5 \cdot 93 \times 10^{-8}$.

It is necessary to remark that, considering the nature of the assumptions made, the numerical agreement in these cases should not be unduly emphasised. It should be considered only as indicating that the effect of the anisotropy of the polarisation field is of the order of magnitude necessary to explain the deviation of Langevin's theory from observation.

An examination of Table I shows that in all cases the influence of the anisotropy of the polarisation field is to diminish the magnitude of the Kerr effect to be expected. On the above assumption of an ellipsoidal cavity this result finds a ready explanation in the fact that the longer geometrical dimension of the molecule—and therefore also of the ellipsoid—almost always goes hand-inhand with the direction of greater electrical or optical polarisability of the molecule.

6. Summary.

In this paper a new theory of electric and magnetic double refraction in liquids is put forward, which can in essence be regarded as a modification of the Langevin-Born theory. It is assumed in the latter theory that, while the molecules themselves are anisotropic, their distribution round any particular molecule in the medium can be considered as being spherically symmetrical with respect to it. This assumption can hardly be correct in any actual liquid, so that the local polarisation field acting on any molecule must depend on its orientation. The Langevin-Born theory is accordingly modified so as to take this "anisotropy" of the polarisation field also into account. The modified expression for birefringence is in better accord with facts than the Langevin-Born expression. As a rule the effect of the "anisotropy" of the polarisation field is to diminish the magnitude of the birefringence to be expected. This is explicable as due to the fact that, in general, the longer linear dimension of a molecule tends to be also the direction of maximum electrical and optical susceptibility. The distribution of the molecules in a dense fluid therefore tends to be such that their mutual influence is equivalent to an apparent diminution in the anisotropy of the molecules.

Density of the Vapour in the Mercury Arc and the Relative Intensities of the Radiated Spectral Lines, with Special Reference to the Forbidden Line 2270.

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[Plates 1-3.]

Introduction.

The mercury arc line $(1 \, {}^{1}S_{0} - 2 \, {}^{3}P_{2})^{*}$ is ruled out by the selection principle as the transition $2 \, {}^{3}P_{2} \rightarrow 1 \, {}^{1}S_{0}$ involves a change of the inner quantum number by 2. Takamine and Fukuda,[†] however, have detected this line in the end-on radiation from a mercury vapour lamp of "the branched arc" type devised by Dr. Metcalfe and the author[‡] for the study of selective absorption in luminous mercury vapour. Foote, Takamine and Chenault§ have obtained the same result using an arc discharge in mercury vapour with a hot cathode. Takamine|| has recently studied the intensity variations of this line with change of current

^{*} Notation.—The number to the upper left of each term symbol represents the multiplicity, and the subscript to the right the inner quantum number. The lowest term number for each class of terms is that adopted by Paschen and Götze.

^{† &#}x27;Phys. Rev.,' vol. 25, p. 23 (1925).

^{‡ &#}x27;Roy. Soc. Proc.,' A, vol. 100, p. 152 (1922).

^{§ &#}x27;Phys. Rev.,' vol. 26, p. 165 (1925).

^{|| &#}x27; Z. f. Physik,' vol. 37, p. 72 (1926).