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The experiment described above offers good conditions for such an observation since a brief electric discharge is sent through H_2O_2 vapor and then the partly decomposed vapor is pumped out and replaced by fresh vapor so that the OH band observed is certain to originate from dissociating H_2O_2 .

A comparison of the OH bands in H_2O and H_2O_2 actually shows a distinct difference in abnormal rotation. For equal intensities at the low rotational lines in H_2O_2 , the tail representing the highest rotation is more intense than in H_2O . This result confirms the idea of the origin of abnormal rotation of OH.

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Solvent Action on Optical Rotatory Power

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A general theory of the optical rotatory power of liquids is developed. The method of C. G. Darwin, supplemented so that the fundamental quantities $s_{\alpha\beta\gamma}\dots$ † which appear there are related to the properties of the molecules comprising the medium, is followed. The optical properties of a molecule are given by a set of tensors $\sigma'_{\alpha\beta\gamma}\dots$. The concept of deformation leads naturally to a simple relation between the $\sigma'_{\alpha\beta\gamma}\dots$'s and the field acting on the molecule. The electrostatic field of the dipoles of the surrounding mole-

cules is computed for the limiting cases of imperfect gases and dilute solutions, for molecules of simple geometrical configuration. This field is identified with the solvent field. For these idealized systems, the rotatory power of a molecule in various solvents is determined in terms of quantities characteristic of the solvents. The resulting equations are controlled by comparing with the behavior of actual liquids.

SECTION 1

THE problem of the solvent action on optical rotatory power dates back to within a few years of the discovery of natural gyration itself by Biot.¹ His early work on solutions (1815–1832) led Biot² to invent the quantity “specific rotation” which he believed to be characteristic for a particular optically active substance. He concluded from these experiments that each molecule possesses the property of rotating the plane of polarized light a definite amount and that “the active molecules (solute) merely disperse themselves among the inactive molecules (solvent), as if in free space, without suffering from them any action which modifies their rotatory power appreciably.”³ In subsequent experiments however, it was found that all active substances show variations of specific rotation with solvent, concentration and temperature.

The earliest explanation of this solvent action,

* Adapted from a dissertation submitted to Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† $s_{\alpha\beta\gamma}\dots$ in Darwin's notation.

¹ J. B. Biot, *Mém. acad. sciences* **15**, 93 (1838).

² J. B. Biot, *Mém. acad. sciences* **13**, 39 (1835).

³ J. B. Biot, *Ann. chim. phys.* (3) **36**, 258 (1852).

the tautomerism theory, was closely associated with anomalous rotatory dispersion. Historically, the tautomerism theory arose from studies on tartaric acid. Biot found that tartaric acid solutions not only exhibited a strong solvent effect, but also showed anomalous rotatory dispersion, so-called because the dispersion curve showed a maximum in the visible region. He artificially produced the dispersion anomaly by measuring simultaneously two substances with simple dispersion but opposite rotations.⁴ This suggestive idea was explicitly formulated, and applied to the solvent effect, by Arndtsen⁵ in 1858. He concluded that anomalous dispersion is caused by the existence of two forms of tartaric acid in solution, varying proportions of the two forms being responsible for the changes of rotation with concentration. The variation of the proportions was later considered to be due to a shift in an equilibrium between the two forms.⁶

Confirmation of the existence of tautomers was obtained from the work on mutarotation in

⁴ J. B. Biot, *Comptes rendus* **2**, 543 (1836).

⁵ A. Arndtsen, *Ann. chim. phys.* (3) **54**, 403 (1858).

⁶ T. M. Lowry and T. W. Dickson, *Trans. Faraday Soc.* **10**, 96 (1914); T. M. Lowry and P. C. Austin, *Phil. Trans. Roy. Soc. A222*, 249 (1922).

sugars and on enol-keto isomerism, principally late in the 19th century. The theory was further developed by Armstrong and Walker⁷ who showed by means of their "characteristic diagrams" that compounds with simple rotatory dispersion could also be interpreted as existing in two tautomeric forms. Latterly, Lucas⁸ has generalized the theory by postulating an arbitrary number of tautomers (three for tartaric acid and its esters), and has explained the shift in equilibrium by an interaction between the solvent and each form.

The work of Kuhn,⁹ however, has shown that all active compounds must exhibit anomalous rotatory dispersion. The distinction between anomalous rotatory dispersion and simple rotatory dispersion depends, therefore, on a fortuitous choice of spectral regions. The building up of "anomalous" dispersion from two or more "simple" dispersions thus has no physical significance.

While compounds with known tautomers like sugars, enol-keto types, and nitrocamphor adjust their equilibria only over considerable periods of time, following the course of the overwhelming majority of organic reactions, the compounds for which tautomerism is the explanation of the solvent effect show no suspicion of a finite rate of change of rotation. Thus the only proof of the existence of tautomers of these latter compounds is the optical evidence which the tautomers are called upon to explain.

Parallel to the development of the tautomerism theory there arose the somewhat vague concept of deformation to account for the small and not very spectacular changes of rotation of the majority of active compounds. Attempts were made to correlate these changes with internal pressure, changes of molecular size, and so forth; in general, with little success. This idea of deformation was not clearly distinguished from the equally vague ideas of solvation or association.^{10, 11}

The above theories, developed when our knowledge of the physical basis of optical rotatory power was small, have failed to give a satisfactory account of the general phenomenon. In view of the criticism^{12, 13} to which they are subject, it is clear that we must turn to the modern theories for an explanation of the solvent effect.

With the advent of the electronic theories of optical rotatory power came the realization that the fundamental quantity describing optical activity was not the specific rotation, but a quantity of the form

$$[\alpha]/f(n),$$

where n is the refractive index of the medium.¹⁴⁻¹⁸ The generally accepted value $n^2 + 2$ for $f(n)$ found by Gans in his correction of Born's theory, we have confirmed by a more precise derivation from Darwin's general theory.¹⁹ The expression

$$[\alpha]/n^2 + 2 \equiv \Omega$$

bears the same relation to specific rotation as refractivity does to refractive index. We shall, therefore, call it the "rotivity." Experimental attempts have been made to establish the invariance of this quantity, without much success. The experiments of Wolf and Volkmann²⁰ indicated the reason for this. They found that the law, $\Omega = \text{constant}$, was obeyed by systems without dipoles but not by those with dipoles.

The concept of deformation has recently been reestablished on a firm theoretical foundation by de Malleman¹⁶ and Kuhn.⁹ They demonstrated that a minute variation in the position of the virtual oscillators will produce a very large change in rotatory power. This viewpoint, together with an exact specification of the external influence producing the displacement, in terms of the electric moments of the solvent molecules, forms the basis of the theory of solvent action developed in this paper. With the aid of these

¹² G. Bruhat, *Trans. Faraday Soc.* **30**, 410, 428 (1930).

¹³ T. S. Patterson, *Nature* **136**, 454 (1935).

¹⁴ M. Born, *Physik. Zeits.* **16**, 251 (1915); *Ann. d. Physik* (4) **55**, 177 (1917).

¹⁵ R. Gans, *Zeits. f. Physik* **27**, 164 (1924); *Ann. d. Physik* (4) **79**, 547 (1926).

¹⁶ R. de Malleman, *Ann. d. physique* (10) **2**, 170 (1924).

¹⁷ G. H. Livens, *Phil. Mag.* **25**, 817 (1913).

¹⁸ S. F. Boys, *Proc. Roy. Soc. A* **144**, 655 (1934).

¹⁹ C. G. Darwin, *Trans. Camb. Phil. Soc.* **23**, 137 (1924).

²⁰ K. L. Wolf and H. Volkmann, *Zeits. f. physik. Chemie* **B3**, 139 (1929); H. Volkmann, *ibid.* **B10**, 161 (1930).

⁷ H. E. Armstrong and E. E. Walker, *Proc. Roy. Soc. A* **88**, 388 (1913).

⁸ R. Lucas, *Trans. Faraday Soc.* **30**, 418 (1930).

⁹ W. Kuhn, *Zeits. f. physik. Chemie* **B4**, 14 (1929); W. Kuhn and E. Braun, *ibid.* **B8**, 281 (1930); W. Kuhn and K. Freudenberg, *Hand- und Jahrbuch der chemischen Physik*, **8**, part 3 (Akadem. Verlagsges. M. B. H., Leipzig, 1932).

¹⁰ C. Winther, *Zeits. f. physik. Chemie* **60**, 590 (1907).

¹¹ T. S. Patterson, *J. Chem. Soc.* **103**, 145 (1913).

two simple concepts, we will find it possible to give a unified quantitative explanation of all the phenomena, as well as empirical formulae, that constitute the solvent effect.

SECTION 2

The analysis of C. G. Darwin¹⁹ refers the optical properties of a continuous medium to a set of constants $s_{\alpha\beta}$, $s_{\alpha\beta\gamma}$, \dots , which are the coefficients of the expansion of the Hertzian vector Π_α of a material element dV in terms of derivatives of R

$$\Pi_\alpha = \frac{E_\beta dV}{4\pi} \left\{ s_{\alpha\beta} + \frac{1}{k} s_{\alpha\beta\gamma} \frac{\partial}{\partial x_\gamma} + \dots \right\} R, \quad (1)$$

where $E_\beta e^{ikct}$ is the radiation field due to everything but a small sphere about dV , and

$$R = e^{ik(ct-r)}/r.$$

(The $s_{\alpha\beta}\dots$ [and the $\sigma_{\alpha\beta}\dots$] are tensors. The subscripts refer to the tensor components and have the values 1, 2 or 3. The summation convention is used throughout.)

We will refer the $s_{\alpha\beta}\dots$ to quantities characteristic of the molecules comprising the medium; that is, perform the transition from the actual assemblage of molecules to the ideal continuous medium.

Let $\Delta\tau$ be a small volume element of a fluid, containing N_j molecules of type j ($j=1, 2, \dots, n$). If $E_\beta^m e^{ikct}$ be the actual radiation field on the m th molecule, it will set up a wavelet specified by

$$p_\alpha^m = \frac{E_\beta^m}{4\pi} \left\{ \sigma_{\alpha\beta}^m + \frac{1}{k} \sigma_{\alpha\beta\gamma}^m \frac{\partial}{\partial x_\gamma} + \dots \right\} R^m, \quad (2)$$

$$\text{where } R^m \equiv \frac{e^{ik(ct-r^m)}}{r^m};$$

$$r^m = [(x_\alpha^m - x_\alpha)^2]^{1/2} = [(x_\alpha^0 - x_\alpha) + \Delta^m x_\alpha^0]^2]^{1/2}.$$

The effect at x_α of the entire element is given by the Hertzian vector

$$\Pi_\alpha = \sum_{j=1}^n \Pi_\alpha^j \quad (3)$$

where Π_α^j , the contribution to Π_α from molecules of type j , is

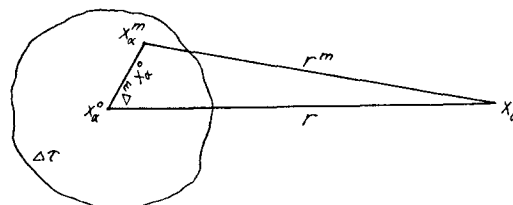


FIG. 1.

$$\Pi_\alpha^j = \sum_{m=1}^{N_j} p_\alpha^m = \sum_{m=1}^{N_j} \frac{E_\beta^m}{4\pi} \left\{ \sigma_{\alpha\beta}^m + \frac{1}{k} \sigma_{\alpha\beta\gamma}^m \frac{\partial}{\partial x_\gamma} + \dots \right\} R^m. \quad (4)$$

Now

$$\begin{aligned} f(r^m) &= f(r) + \Delta^m x_\alpha^0 \frac{\partial}{\partial x_\alpha^0} f(r) \\ &\quad + \Delta^m x_\alpha^0 \Delta^m x_\beta^0 \cdot \frac{1}{2!} \frac{\partial^2}{\partial x_\alpha^0 \partial x_\beta^0} f(r) + \dots \\ &= f(r) - \Delta^m x_\alpha^0 \frac{\partial}{\partial x_\alpha} f(r) \\ &\quad + \Delta^m x_\alpha^0 \Delta^m x_\beta^0 \cdot \frac{1}{2!} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} f(r) - \dots, \end{aligned}$$

whenever $f(\rho)$ is analytic for $|\rho| \leq |r^m - r|$. (ρ complex.)

Hence, for x_α outside of $\Delta\tau$

$$R^m = R - \Delta^m x_\gamma^0 \frac{\partial}{\partial x_\gamma} R + \frac{\Delta^m x_\gamma^0 \Delta^m x_\delta^0}{2!} \frac{\partial^2}{\partial x_\gamma \partial x_\delta} R - \dots \quad (5)$$

$$\text{and } E_\beta^m e^{ikct} = A_\beta e^{ik(ct - \mu_\alpha x_\alpha^m)}$$

$$= \{1 + (x_\alpha^m - x_\alpha^0)(-ik\mu_\alpha) + \dots\} E_\beta^0 e^{ikct}. \quad (5')$$

From (4), (5) and (5')

$$\begin{aligned} \Pi_\alpha^j &= \frac{E_\beta^0 + \Delta^m x_\alpha^0 (-ik\mu_\alpha) E_\beta^0 + \dots}{4\pi} \\ &\quad \times \left\{ \sum_{m=1}^{N_j} \sigma_{\alpha\beta}^m + \left[\frac{1}{k} \sigma_{\alpha\beta\gamma}^m - \Delta^m x_\gamma^0 \sigma_{\alpha\beta}^m \right] \frac{\partial}{\partial x_\gamma} + \left[\frac{1}{k^2} \sigma_{\alpha\beta\gamma\delta}^m \right. \right. \\ &\quad \left. \left. - \Delta^m x_\delta^0 \frac{1}{k} \sigma_{\alpha\beta\gamma}^m + \frac{\Delta^m x_\gamma^0 \Delta^m x_\delta^0}{2!} \sigma_{\alpha\beta}^m \right] \frac{\partial^2}{\partial x_\gamma \partial x_\delta} + \dots \right\} R. \end{aligned}$$

Let $\sigma'_{\alpha\beta\gamma}\dots$ be the tensors $\sigma_{\alpha\beta\gamma}\dots$ referred to a set of axes (x_1', x_2', x_3') fixed in the molecule. The equations relating the two sets of axes are:

$$x_\beta' = l_{\alpha\beta} x_\alpha, \quad x_\alpha = l_{\alpha\beta} x_\beta'.$$

Then

$$\sigma'_{\alpha\beta\gamma\delta\dots} = l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} l_{\delta\theta} \dots \sigma'_{\xi\eta\zeta\theta\dots}, \quad (6)$$

where $\sigma'_{\xi\eta\zeta\theta\dots}$ (j) is the same for each of the N_j molecules of type j .

Neglecting interaction

Let (x'_1, x'_2, x'_3) be given with respect to the fixed axes (x_1, x_2, x_3) by the usual Eulerian coordinates. Under the specification that the $\Delta\tau$'s in the medium are precisely alike (this neglects the light scattering which is responsible for the blue of the sky), we set $N_j = n_j \Delta\tau$ where n_j = number of j type molecules per cc. Performing the transition from an actual fluid to a continuous medium,

$$\Delta\tau \rightarrow dV, \quad \Delta^m x \alpha^0 \rightarrow 0$$

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta}^m = \sum_{m=1}^{N_j} l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \sigma'_{\xi\eta} \rightarrow \frac{n_j dV}{8\pi^2} \times \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^\pi l_{\alpha\xi} l_{\beta\eta} \sin \theta d\theta, \quad (7)$$

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta\gamma}^m = \sum_{m=1}^{N_j} l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \sigma'_{\xi\eta\zeta} \rightarrow \frac{n_j dV}{8\pi^2} \sigma'_{\xi\eta\zeta} \times \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^\pi l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \sin \theta d\theta. \quad (8)$$

The integrations in (7) and (8) are straightforward. We find as a result

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta}^m \rightarrow \frac{n_j dV}{3} \sigma'_{\xi\eta}(\xi\eta)(\alpha\beta) \quad (\alpha\beta) = \begin{cases} 0 & \alpha \neq \beta \\ 1 & \alpha = \beta \end{cases} \quad (9)$$

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta\gamma}^m \rightarrow \frac{n_j dV}{6} \sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma], \quad (10)$$

where $[\xi\eta\zeta] = 0$ for all values except

$$[123] = [231] = [312] = -[213] \\ = -[132] = -[321] = +1.$$

The duplicate rule²¹

$$\sigma'_{\alpha\beta\gamma\delta\epsilon\dots}(\theta\zeta) = 0$$

if $(\theta\zeta)$ is $(\beta\gamma)$, $(\beta\delta)$, $(\beta\epsilon)\dots$, $(\gamma\delta)$, $(\gamma\epsilon)\dots$, $(\delta\epsilon)\dots$, \dots , applied to $\Pi_{\alpha'}$, vanishes the remaining coefficients.

²¹ Darwin, reference 19, p. 150.

Putting (9) and (10) into the expression for $\Pi_{\alpha'}$ yields

$$\Pi_{\alpha'} = \frac{E_{\beta^0}}{4\pi} \left\{ \frac{n_j dV}{3} \sigma'_{\xi\eta}(\xi\eta)(\alpha\beta) + \frac{1}{k} \frac{n_j dV}{6} \sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma] \frac{\partial}{\partial x_\gamma} \right\} R. \quad (11)$$

Comparing this with the form (1), and identifying E_{β^0} with E_β ,

$$s_{\alpha\beta} = \sum_{j=1}^n \frac{n_j}{3} \sigma'_{\xi\eta}(\xi\eta)(\alpha\beta) \quad s_{\alpha\beta\gamma\delta} = 0 \quad (12)$$

$$s_{\alpha\beta\gamma} = \sum_{j=1}^n \frac{n_j}{6} \sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma]. \quad (13)$$

It is shown by Darwin that if $s_{\alpha\beta}$ is of the form $s_0(\alpha\beta)$ and $s_{\alpha\beta\gamma}$ of the form $s_1[\alpha\beta\gamma]$, then²²

$$3 \cdot \frac{n^2 - 1}{n^2 + 2} = s_0, \quad (14)$$

$$\alpha = \frac{\pi}{\lambda_{vac.}} \cdot \frac{n^2 + 2}{3} \cdot s_1, \quad \alpha = \text{rotation/cm.} \quad (15)$$

From (13) and (15) we can obtain the fundamental relationships between stereochemistry and optical rotatory power. The rotatory power of a molecule vanishes if and only if

$$\sigma'_1 = \sigma'_{\xi\eta\zeta}[\xi\eta\zeta] = 0. \quad (16)$$

Let G be the group of symmetry operations belonging to the molecule. Each operation in G may be specified by a change of axes. Under an arbitrary change of axes

$$\sigma''_{\alpha\beta\gamma\dots} = l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \dots \sigma'_{\xi\eta\zeta\dots} \quad (17)$$

and under G $\sigma''_{\alpha\beta\gamma\dots} = \sigma'_{\alpha\beta\gamma\dots}$ (18)

Let T be the operation of reflection.

$$T: \quad l_{11} = -1 \quad l_{22} = l_{33} = +1.$$

Denoting the molecule obtained by T by a double prime,

$$\sigma_{123}'' = l_{1\xi} l_{2\eta} l_{3\zeta} \sigma'_{\xi\eta\zeta} = -\sigma_{123}' \text{ etc.}$$

hence

$$\sigma_{11}'' = -\sigma_{11}'.$$

Therefore, two molecules which are mirror images have equal and opposite rotations.²³ If T belongs to G , $\sigma_{11}'' = \sigma_{11}' = 0$. Therefore, a necessary condition that a molecule exhibit natural gyration is that it be nonsuperposable with its mirror image.²⁴

²² Eq. (15), although not written explicitly, follows immediately from (22.2), Darwin, reference 19, p. 162.

²³ L. Pasteur, Comptes rendus 35, 176 (1852).

²⁴ L. Pasteur, Alembic Club Reprints 14, 24.

Similarly, we can show that association is without effect on rotatory power.²⁵

The fundamental Eq. (6) is true only when the effect on the m th molecule of the electrostatic fields of all the other molecules of the medium, \mathbf{F}^m , is neglected. Dropping this restriction, we have, in general

$$\sigma_{\alpha\beta\gamma}^m = l_{\alpha\xi}^m l_{\beta\eta}^m l_{\gamma\zeta}^m \cdots \sigma'_{\xi\eta\zeta} \cdots (\mathbf{F}^m). \quad (19)$$

Eq. (8) is then replaced by

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta\gamma}^m \rightarrow \frac{n_j dV}{8\pi^2} [\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\text{av}} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^\pi \times l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \sin \theta d\theta, \quad (20)$$

where the average is taken over all positions and orientations of all the molecules of the fluid relative to the m th molecule. From (10) and (13)

$$s_{\alpha\beta\gamma} = \sum_{j=1}^n \frac{n_j}{6} [\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\text{av}} [\xi\eta\zeta] [\alpha\beta\gamma]$$

and from (15)

$$\alpha = \frac{\pi}{\lambda_{\text{vac}}} - \frac{n^2 + 2}{3} \sum_{j=1}^n \frac{n_j}{6} [\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\text{av}} [\xi\eta\zeta]. \quad (21)$$

SECTION 3

We know that $\sigma'_{\xi\eta}$, the scattering coefficient which determines the refractivity, varies in a uniform electric or magnetic field according to the law

$$\sigma'_{\xi\eta}(\mathbf{F}) = \sigma'_{\xi\eta}(0) + \sigma'_{\xi\eta}{}^\delta F_\delta + \sigma'_{\xi\eta}{}^{\delta\gamma} F_\delta F_\gamma,$$

the small coefficients $\sigma'_{\xi\eta}{}^\delta$ and $\sigma'_{\xi\eta}{}^{\delta\gamma}$ contributing to the Faraday effect, the Cotton-Mouton effect,

²⁵ Suppose that two molecules, 1 and 2, are associated and move in unison. The contribution to $6s_{\alpha\beta\gamma}$ by these molecules is

$$\{\sigma'_{1\xi\eta\zeta} + \sigma'_{2\xi\eta\zeta}\} [\xi\eta\zeta],$$

choosing as axes for the whole system the axes of molecule 1: $\sigma'_{2\xi\eta\zeta}$ is now the scattering tensor of the 3rd rank of molecule 2 referred to the axes of 1. But, if $l_{\alpha\beta}$ be the direction-cosines of the transformation from the axes of 1 to the axes of 2,

$$\sigma'_{2\xi\eta\zeta} [\xi\eta\zeta] = l_{\xi\alpha} l_{\eta\beta} l_{\zeta\gamma} \sigma'_{2\alpha\beta\gamma} \cdot l_{\xi\theta} l_{\eta\varphi} l_{\zeta\psi} [\theta\varphi\psi] = \sigma'_{2\alpha\beta\gamma} (\alpha\theta) (\beta\varphi) (\gamma\psi) [\theta\varphi\psi] = \sigma'_{2\alpha\beta\gamma} [\alpha\beta\gamma].$$

The contribution to $6s_{\alpha\beta\gamma}$ of the associated pair is then

$$\sigma'_{1\xi\eta\zeta} [\xi\eta\zeta] + \sigma'_{2\xi\eta\zeta} [\xi\eta\zeta],$$

which is precisely the same as that of an unassociated pair. We conclude that association without interaction is without effect on rotatory power, and that a compound built up from optically active compounds without rearrangement or distortion will exhibit optical superposition.

the Kerr effect, and so forth.²⁶ However, the fact that the refractivities are additive in solvent pairs such as heptane-ethyl iodide, $\text{CCl}_4 - \text{CH}_3\text{COCH}_3$, $\text{CCl}_4 - \text{CH}_3\text{COOCH}_3$, and ethyl bromide-ethanol to 0.07 percent,²⁷ indicates that the sources of variation of refractivity are unable to account for the variations of the rotivity of the observable magnitude. The essential feature by which $\sigma'_{\xi\eta\theta} [\xi\eta\theta]$ differs from $\sigma'_{\xi\eta} (\xi\eta)$ is the explicit dependence of the former on the positions of the atoms: $\sigma'_{\xi\eta} (\xi\eta)$ is completely independent of the positions of the atoms, the refractivities of organic compounds being an additive function of the refractivity of the constituent atoms.²⁸

We conclude that the variations of $\sigma'_{\xi\eta\theta} [\xi\eta\theta]$ in solvent fields should be attributed to the changes in position of the atoms. This is precisely the concept of deformation.¹⁶

Accordingly we set

$$\sigma'_{\xi\eta\zeta}(\mathbf{F}) = \sigma'_{\xi\eta\zeta}(\mathbf{q}^1, \mathbf{q}^2, \cdots \mathbf{q}^t) \equiv \sigma'_{\xi\eta\zeta}(\mathbf{q}^k),$$

where \mathbf{q}^k is the position vector of the k th atom with respect to an arbitrary origin in the molecule, and

$$\mathbf{q}^k = \mathbf{q}_0^k + \mathbf{u}^k(\mathbf{F})$$

$\mathbf{u}^k(\mathbf{F})$ being the displacement of the k th atom from rest under influence of the uniform external field \mathbf{F} . Then

$$\sigma'_{\xi\eta\zeta}(\mathbf{q}^k) = \sigma'_{\xi\eta\zeta}(\mathbf{q}_0^k) + \frac{\partial \sigma'_{\xi\eta\zeta}(\mathbf{q}_0^k)}{\partial q_{0\alpha}^s} u_\alpha^s + \cdots,$$

discarding higher terms on the assumption that \mathbf{u} is small. We assume that $u_\alpha^s = \varphi_{\alpha\delta}^s F_\delta$, where $\varphi_{\alpha\delta}^s$ is the deformability tensor for the s th particle. Then

$$\sigma'_{\xi\eta\zeta}(\mathbf{q}^k) = \sigma'_{\xi\eta\zeta}(\mathbf{q}_0^k) + \left\{ \frac{\partial \sigma'_{\xi\eta\zeta}(\mathbf{q}_0^k)}{\partial q_{0\alpha}^s} \varphi_{\alpha\delta}^s \right\} F_\delta$$

or, returning to the F notation

$$\sigma'_{\xi\eta\zeta}(\mathbf{F}) = \sigma'_{\xi\eta\zeta}(0) + \sigma'_{\xi\eta\zeta}{}^\delta F_\delta \quad (22)$$

$$\text{with} \quad \sigma'_{\xi\eta\zeta}{}^\delta \equiv \frac{\partial \sigma'_{\xi\eta\zeta}(\mathbf{q}_0^k)}{\partial q_{0\alpha}^s} \varphi_{\alpha\delta}^s. \quad (23)$$

²⁶ M. Born *Optik* (Springer, Berlin, 1933), p. 346, Eq. (4), also Sec. 78, 79, 80.

²⁷ C. P. Smyth, E. W. Engel and E. B. Wilson, J. Am. Chem. Soc. 51, 1736 (1929).

²⁸ F. Eisenlohr, *Spektrochemie Organische Verbindungen* (F. Enke, Stuttgart, 1912).

If the field is nonuniform, the F_δ must be interpreted as the field at some fiducial point in the molecule, and other terms in $\partial F_\delta/\partial x_\beta$, $\partial^2 F_\delta/\partial x_\beta \partial x_\gamma$, and so forth, must be added to the right of (22). We take no further notice of these terms since they will be shown to contribute nothing to $[\sigma_{\xi\eta\theta}'(\mathbf{F})]_{\text{av}}$.

We note that the above considerations are consistent with the work of Kuhn,²⁹ who relates solvent changes of rotation with changes in the anisotropy of the circularly dichroic absorption bands. The latter, according to Kuhn's theory³⁰ are directly connected with changes in the atomic distances and angles.

For a system containing only one optically active substance we obtain from (21) and (22) an expression for the rotatory power, namely,

$$\alpha = \frac{\pi}{\lambda_{\text{vac}}} \cdot \frac{n^2 + 2}{3} \cdot \frac{n_j}{6} \{ \sigma'_{\xi\eta\zeta}(0) + \sigma'_{\xi\eta\zeta}{}^\delta(F_\delta)_{\text{av}} \} [\xi\eta\zeta]. \quad (24)$$

Since $(F_\delta)_{\text{av}}$ is (Section 4) of the order 10^3 e.s.u., $\sigma'_{\xi\eta\theta}{}^\delta$ need be only 0.01 percent of $\sigma'_{\xi\eta\theta}(0)$ for a 10 percent change in rotatory power. The second term in $\{\}$ is responsible for the change of rotation with solvent. $\sigma'_{\xi\eta\theta}{}^\delta$ need not be of the same sign as $\sigma'_{\xi\eta\theta}(0)$. If $\sigma'_{\xi\eta\theta}(0)$ should be small, and $\sigma'_{\xi\eta\theta}{}^\delta$ of the opposite sign, for some values of $(F_\delta)_{\text{av}}$ the rotation will be positive, for others, negative.

According to Kuhn's theory^{9, 30}, for example, the actual expression for $\sigma'_{\xi\eta\theta}(0)[\xi\eta\theta]$ is of the form $\sum_i (A_i/(\lambda_i^2 - \lambda^2))$, where A_i depends on the intramolecular distances and angles. Thus $\sigma'_{\xi\eta\theta}{}^\delta[\xi\eta\theta]$ is of the form $\sum_i (B_i/(\lambda_i^2 - \lambda^2))$. In spectral regions where one Drude term suffices, the dispersion of $\sigma'_{\xi\eta\theta}{}^\delta[\xi\eta\zeta]$ is the same as the dispersion of $\sigma'_{\xi\eta\theta}(0)[\xi\eta\zeta]$; if more than one Drude term is required, the dispersions will be different.

Eq. (24) shows that the rotivity is the sum of the contributions of two terms whose relative magnitude is variable. Therefore, optically active substances behave as if there are two substances (in general, with different dispersions) present in solution. Consequently, the graphical analyses³¹ and correlations of data based on the assumption

²⁹ W. Kuhn, K. Freudenberg and R. Seidler, *Zeits. f. physik. Chemie* **B13**, 379 (1931).

³⁰ W. Kuhn and K. Bein, *Zeits. f. physik. Chemie* **B22**, 406 (1933).

³¹ T. M. Lowry, *Optical Rotatory Power* (Longmans, Green & Co., London, 1935), Chap. 32.

of tautomers can equally well be accounted for by the concept of deformation. The fact that the variations in rotatory power with temperature fall on the same "characteristic diagram" as those caused by solvents,³² indicates that the temperature effect is only an indirect solvent effect. (See Section 7, part I.D.)

It has also been noticed that a series of related compounds have the same "characteristic diagram."³³ This effect can by no means be explained in terms of tautomers. If we let $\sigma'_{\xi\eta\theta}[\xi\eta\theta] \times \text{constant}$ represent the contribution to the rotivity of a single circularly-dichroic absorption band common to all the compounds, then this can be split up into

$$\text{constant} \times \{ \sigma'_{\xi\eta\zeta}(0) + \sigma'_{\xi\eta\zeta}{}^\delta(F_\delta)_{\text{av}} \} [\xi\eta\zeta]$$

as before, with $(F_\delta)_{\text{av}}$ now representing the average field of the rest of the molecule. The "vicinal action" of the substituent groups, therefore, in no wise differs, except possibly in magnitude, from the solvent action. If the substituent group is polar and free to rotate, $(F_\delta)_{\text{av}} \sim \mu^2/3kT$ (Section 6). Such an experimental relationship between $[\alpha]$ and the polarity of the substituent group has already been found by Betti.³⁴

SECTION 4

Eq. (24) shows that the change of rotivity depends on the vector value of F_δ .³⁵ Only those fields whose average components on the $(x_1'x_2'x_3')$ set of axes do not vanish will contribute to the change of rotivity. If the motion of a molecule with respect to the $(x_1'x_2'x_3')$ set of axes is random, the field of the solvent molecule will have no effect no matter what the field may be. Therefore, the whole of the solvent fields measured by the change in rotivity will be the result of deviations from random distribution (with respect to the solute molecules) of the solvent molecules caused by the solute molecules.

With this in mind, we consider the limiting case where the solvent is a continuous medium.³⁶ We suppose the molecule to occupy a spherical cavity C (of radius a) in a continuous infinite medium of dielectric constant ϵ . Let $V(r, \theta, \psi)$ be the potential function of the molecule. As a

³² T. S. Patterson, *J. Chem. Soc.* **109**, 1176 (1916).

³³ R. H. Pickard and J. Kenyon, *J. Chem. Soc.* **105**, 844, 1118, 2269 (1914).

³⁴ M. Betti, *Trans. Faraday Soc.* **30**, 337 (1930).

³⁵ Therefore, the work of Holtsmark [J. Holtsmark, *Ann. d. Physik* (4) **58**, 577 (1919); *Physik. Zeits.* **25**, 79 (1924)], who computed the probability function for the scalar values of F to account for the broadening of spectral lines by foreign gases, does not apply.

³⁶ F. C. Frank, *Proc. Roy. Soc. A* **152**, 171 (1935); K. Higasi, *Sci. Papers Inst. Phys. Chem. Research* **28**, 284 (1936).

result of the field of the molecule, a distribution of charge is induced on the walls of the cavity; the field of this charge distribution is the solvent field. Let U be the potential of the dielectric. Let U_i be the function U inside C , U_0 the function U outside C . Supposing V unaltered by the fields of dielectric, U satisfies the following schedule of conditions:³⁷

$$\begin{aligned} \nabla^2 U &= 0, \quad [U_0]_{r=a} = [U_i]_{r=a}, \\ \epsilon \left[\frac{\partial U_0}{\partial r} \right]_{r=a} - \left[\frac{\partial U_i}{\partial r} \right]_{r=a} &= (1-\epsilon) \left[\frac{\partial V}{\partial r} \right]_{r=a}, \\ [U_i]_{r=0} &= \text{finite}; \quad [U_0]_{r=\infty} = 0. \end{aligned} \quad (25)$$

Let V be the potential of a permanent electric dipole \mathbf{u} at 0.

$$V = \frac{\mathbf{u} \cdot \mathbf{r}}{r^3} = \frac{\mu \cos \theta}{r^2}, \quad (26)$$

$$\begin{aligned} U_i &= -\frac{2\mu}{a^3} \left(\frac{\epsilon-1}{2\epsilon+1} \right) \cdot r \cos \theta = -\frac{2\mu z}{a^3} \left(\frac{\epsilon-1}{2\epsilon+1} \right), \\ U_0 &= -2\mu \left(\frac{\epsilon-1}{2\epsilon+1} \right) \frac{\cos \theta}{r^2} \end{aligned} \quad (27)$$

satisfy (25) and represent the potential of the dielectric. The solvent fields are

$$\begin{aligned} F_x &= -\frac{\partial}{\partial x} U_i = 0, \quad F_y = -\frac{\partial}{\partial y} U_i = 0, \\ F_z &= -\frac{\partial}{\partial z} U_i = \frac{2\mu}{a^3} \left(\frac{\epsilon-1}{2\epsilon+1} \right). \end{aligned} \quad (28)$$

This equation agrees with the two experimental facts:

- (i) The rotivity is constant for solutes with no dipole moment but varies widely for solutes with dipole moments.²⁹
- (ii) The change in rotivity of a given compound in various solvents is a function of the dielectric constant of the solvent,³⁸ or, otherwise stated, depends on the polarity of the solvent.³⁹

Two points are important in the above formulae: first, \mathbf{F} is uniform over the entire molecule, and second, \mathbf{F} is additive as far as the dipole of the active molecule is concerned. The former justifies the dropping of the gradient terms in (22); in what is to follow we will assume the field to be uniform over the molecule, and will only evaluate it at the center of the molecule. (Compare Holtsmark³⁵.)

This treatment, although helpful intuitively, is subject to serious objections. A solvent is not a continuous medium. The dielectric constant defines the electrical properties of a medium only for gross quantities and large dimensions: it cannot take account of the fact that a substance like *p*-dinitro benzene, for example, acts like a strongly polar substance, although its moment is zero. We therefore turn to a statistical treatment.

SECTION 5

For simplicity we consider only the case of a 3-component system: composed of an active compound and two inactive compounds. The

partition function for the potential energy of the assembly is^{40, 41}

$$\begin{aligned} B(\vartheta) &= \int \cdots \int_{\text{all accessible phase space}} \vartheta^W \Pi_k(d\omega)^{N_k}, \\ \Pi_k(d\omega)^{N_k} &\equiv \prod_{r=1}^{N_\alpha} d\omega_{\alpha r} \prod_{s=1}^{N_\beta} d\omega_{\beta s} \prod_{t=1}^{N_\gamma} d\omega_{\gamma t} \\ d\omega_{\alpha r} &= (dx_\alpha dy_\alpha dz_\alpha \sin \theta_\alpha d\theta_\alpha d\varphi_\alpha d\psi_\alpha)_r \\ &\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \end{aligned}$$

where $x_\alpha, y_\alpha, z_\alpha$ are the Cartesian coordinates and $\theta_\alpha, \varphi_\alpha, \psi_\alpha$ the Eulerian coordinates of an α -molecule referred to some arbitrary system of axes. There are similar expressions for $d\omega_{\beta s}$ and $d\omega_{\gamma t}$. $\vartheta = \exp(-1/kT)$ and W is the potential energy of the whole assembly. The electrostatic field of all the other molecules acting on a given α -molecule is

$$F_\delta = \sum_{r=2}^{N_\alpha} F_{(\alpha r)\delta} + \sum_{s=1}^{N_\beta} F_{(\beta s)\delta} + \sum_{t=1}^{N_\gamma} F_{(\gamma t)\delta}, \quad (29)$$

where $F_{(\beta s)\delta}$ is the δ -component ($\delta=1, 2, 3$) (corresponding to three Cartesian axes in the chosen α -molecule) of the field of the s th β -molecule at the chosen α -molecule. The average field is given by

$$[F_\delta]_{\text{av}} = \int \cdots \int F_\delta \vartheta^W \Pi_k'(d\omega)^{N_k} / B'(\vartheta), \quad (30)$$

where $\Pi_k'(d\omega)^{N_k} d\omega_{\alpha 1} = \Pi_k(d\omega)^{N_k}$

and $\int d\omega_{\alpha 1} B'(\vartheta) = B(\vartheta)$.

We have

$$[F_\delta]_{\text{av}} = F_{(1)\delta} + F_{(2)\delta} + F_{(3)\delta}, \quad (31)$$

where

$$F_{(1)\delta} \equiv \int \cdots \int \sum_{r=2}^{N_\alpha} F_{(\alpha r)\delta} \vartheta^W \Pi_k'(d\omega)^{N_k}, \quad (32)$$

$$F_{(2)\delta} \equiv \int \cdots \int \sum_{s=1}^{N_\beta} F_{(\beta s)\delta} \vartheta^W \Pi_k'(d\omega)^{N_k}, \quad (33)$$

$$F_{(3)\delta} \equiv \int \cdots \int \sum_{t=1}^{N_\gamma} F_{(\gamma t)\delta} \vartheta^W \Pi_k'(d\omega)^{N_k}. \quad (34)$$

It remains to evaluate these integrals.

³⁷ M. Mason and W. Weaver, *The Electromagnetic Field* (University of Chicago Press, Chicago, 1929), p. 146.

³⁸ P. Walden, *Ber. d. Phys. Ges.* **38**, 345 (1905).

³⁹ H. G. Rule and A. McLean, *J. Chem. Soc.* 1400 (1932).

⁴⁰ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1929), Chap. VIII.

⁴¹ J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

Case I

The assembly is an imperfect gas. We evaluate only $F_{(3)\delta}$, the others follow *mutatis mutandi*. Since W is symmetrical in all the N_γ γ -molecules

$$F_{(3)\delta} = N_\gamma \int \cdots \int F_{(\gamma)\delta} \vartheta^W \Pi_k'(d\omega)^{N_k} / B'(\vartheta), \quad (35)$$

dropping the now superfluous subscript (t). $F_{(\gamma)\delta}$ depends, to good approximation, only on the relative coordinates of the chosen α and γ -molecules: thus

$$F_{(3)\delta} = \frac{N_\gamma \int F_{(\gamma)\delta} d\omega_\gamma \int \vartheta^W \Pi_k''(d\omega)^{N_k}}{\int d\omega_\gamma \int \vartheta^W \Pi_k''(d\omega)^{N_k}}. \quad (36)$$

The inner integral^{40, 41} is $Q\vartheta^{E_{\alpha\gamma}}$ where $E_{\alpha\gamma}$ is the interaction energy of the chosen α and γ -molecules. Now

$$\int d\omega_\gamma Q\vartheta^{E_{\alpha\gamma}} \sim Q8\pi^2 V$$

where V is the volume of the system. Hence, finally

$$F_{(3)\delta} = \frac{N_\gamma}{8\pi^2 V} \int \vartheta^{E_{\alpha\gamma}} F_{(\gamma)\delta} d\omega_\gamma. \quad (37)$$

Choosing as our arbitrary system of axes those of the α -molecule, $(N_\gamma/8\pi^2 V)\vartheta^{E_{\alpha\gamma}}d\omega_\gamma$ represents the average number of γ -molecules at a given distance from, and with a particular orientation with respect to the chosen α -molecule in an element of extension $d\omega_\gamma$, and $F_{(\gamma)\delta}$ the field of a single γ -molecule satisfying these conditions, at the origin of the system of coordinates. The integral, which is extended over all possible values of $(x_\gamma, y_\gamma, z_\gamma, \theta_\gamma, \varphi_\gamma, \psi_\gamma)$ is thus the sum of the fields of all the γ -molecules in their average distribution.

Case II

The assembly is a liquid. N_γ is in dilute solution. We consider the experiment of replacing β -molecules with γ -molecules, V and N_α held constant. The β -molecules are supposed nonpolar, the α and γ , polar. $F_{(1)\delta}$ will *not* be invariant, but

will be slowly varying with respect to $F_{(3)\delta}$. $F_{(2)\delta}$ is of course a function of N_β . We set

$$F_{(1)\delta} + F_{(2)\delta} = g_{(\gamma)\delta}(N_\beta),$$

where $g_{(\gamma)\delta}(N_\beta)$ is a smoothly varying function: the subscript γ signifies that the functions g will in general be different for differing molecules γ . Let $W = W_1 + W_2$, where W_1 is not a function of the coordinates of any of the γ -molecules. (35) becomes

$$F_{(3)\delta} = \frac{N_\gamma \int \vartheta^{W_1} \prod_{r=2}^{N_\alpha} d\omega_{\alpha r} \int \prod_{s=1}^{N_\beta} d\omega_{\beta s} \int \vartheta^{W_2} F_{(\gamma)\delta} \prod_{t=1}^{N_\gamma} d\omega_{\gamma t}}{\int \vartheta^{W_1} \prod_{r=2}^{N_\alpha} d\omega_{\alpha r} \int \prod_{s=1}^{N_\beta} d\omega_{\beta s} \int \vartheta^{W_2} \prod_{t=1}^{N_\gamma} d\omega_{\gamma t}}.$$

As a first approximation we suppose $F_{(\gamma)\delta}$ depends only on the relative coordinates of the chosen α -molecule and the γ -molecule. The first approximation to

$$\int \vartheta^{W_2} F_{(\gamma)\delta} \prod_{t=1}^{N_\gamma} d\omega_{\gamma t}$$

$$\text{is then } (8\pi^2 V)^{N_\gamma-1} \int \vartheta^{E_{\alpha\gamma}} F_{(\gamma)\delta} d\omega_\gamma,$$

$$\text{and to } \int \vartheta^{W_2} \prod_{t=1}^{N_\gamma} d\omega_{\gamma t}$$

is $(8\pi^2 V)^{N_\gamma}$, for small N_γ .⁴²

Therefore, finally

$$[F_\delta]_{av} = g_{(\gamma)\delta}(N_\beta) + N_\gamma \frac{\int \vartheta^{E_{\alpha\gamma}} F_{(\gamma)\delta} d\omega_\gamma}{8\pi^2 V}. \quad (38)$$

SECTION 6

The factors that enter into the evaluation of

$$(N_\gamma/8\pi^2 V) \int F_{(\gamma)\delta} \vartheta^{E_{\alpha\gamma}} d\omega_\gamma \quad (39)$$

are the fields and the geometrical shape⁴³ of the individual molecules. We evaluate the integral under the following assumptions:

⁴² R. H. Fowler, reference 40, Chap. XIII.

⁴³ J. Weigle, *Helv. Phys. Acta* **6**, 68 (1933).

(i) Both molecules are uniformly polarizable spheres with dipoles at the center.

(ii) The effective radii of these spheres are such that $kT > 5E_{\alpha\gamma}$.

As far as the active substance (the α -molecule) is concerned, the shape is generally so complicated that the assumption above is the best we can make. Provided the dipoles of the molecules are close together and close to the active carbon atom, it is probably legitimate to add the dipoles and consider them as one single dipole. The electrostatic field of solvent molecules with many dipoles such as 3-nitro-4-amino benzene sulfonic acid cannot be represented as the field of the sum of the dipoles except at distances roughly 10 times the molecular diameter: assumption (i) does not, therefore, correspond to solvent molecules possessing more than a single dipole. The best correspondence will result if the molecules have forms *related* to a sphere with a dipole at the center—such as ellipsoids with a dipole at one focus. In this class the normal alkyl derivatives and the monosubstituted benzene series fall.

For solvent molecules of different shapes, a different assumption (i) must be made: correspondingly the integral will be a different function.⁴⁴

Molecules with a benzenoid nucleus make an added contribution to the solvent field. This field must be practically the same for all aromatic compounds and remain constant in experiments under Case I in which one aromatic compound is replaced by another; therefore, this field does not manifest itself in such experiments and can be ignored. It does, however, cause a separation in the properties of compounds of the aliphatic and those of the aromatic series. In experiments under Case II, this field is added to $g_{(\gamma)\delta}(N_\beta)$. We shall show experimentally that the field is smoothly varying, so that no difficulty results from such a procedure.

Let A , B , and C be the polarizabilities of the α , β and γ -molecules, respectively; \mathbf{F}_α , the field of the α -molecule at the γ -molecule; \mathbf{F}_γ , the field of the γ -molecule at the α -molecule; $F_{(3)1}$, $F_{(3)2}$, $F_{(3)3}$, the components of the average field, $\mathbf{F}_{(3)}$, contributed by all the γ -molecules, in a set of rectangular Cartesian coordinates (i , j , k) fixed in the α -molecule; $\mathbf{u}_\alpha = \mu_\alpha \mathbf{k}$, \mathbf{u}_β , \mathbf{u}_γ the dipole

moments of the α , β , and γ -molecules, respectively; \mathbf{p}_α and \mathbf{p}_γ the induced dipoles of the α and γ -molecules. If \mathbf{r} is the position vector from O , the center of an α -molecule, to P , the center of a γ -molecule, then

$$\mathbf{F}_\alpha = -\frac{\mathbf{u}_\alpha + \mathbf{p}_\alpha}{r^3} + \frac{3\mathbf{r}\mathbf{r} \cdot (\mathbf{u}_\alpha + \mathbf{p}_\alpha)}{r^5},$$

$$\mathbf{F}_\gamma = -\frac{\mathbf{u}_\gamma + \mathbf{p}_\gamma}{r^3} + \frac{3\mathbf{r}\mathbf{r} \cdot (\mathbf{u}_\gamma + \mathbf{p}_\gamma)}{r^5}.$$

Further $\mathbf{p}_\alpha = A\mathbf{F}_\gamma$, $\mathbf{p}_\gamma = C\mathbf{F}_\alpha$.

These four equations determine \mathbf{p}_α and \mathbf{p}_γ : under assumption (ii) the factors A/r^3 and C/r^3 are less than 0.02, so that, to about 2 percent

$$\mathbf{p}_\alpha = -\frac{A\mathbf{u}_\gamma}{r^3} + \frac{3A\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\gamma)}{r^5},$$

$$\mathbf{p}_\gamma = -\frac{C\mathbf{u}_\alpha}{r^3} + \frac{3C\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\alpha)}{r^5}$$

$$\text{and } \mathbf{F}_\gamma = -\frac{\mathbf{u}_\gamma}{r^3} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\gamma)}{r^5} + \frac{C\mathbf{u}_\alpha}{r^6} + \frac{3C\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\alpha)}{r^8}.$$

The interaction energy is

$$-(\mathbf{u}_\alpha + \mathbf{p}_\alpha) \cdot \mathbf{F}_\gamma + Q_\alpha + Q_\gamma,$$

where $Q_\alpha + Q_\gamma$ is the sum of the internal energies of deformation of α and γ . This is⁴⁵ $\frac{1}{2}\mathbf{p}_\alpha \cdot \mathbf{F}_\gamma + \frac{1}{2}\mathbf{p}_\gamma \cdot \mathbf{F}_\alpha$. Hence to the same approximation as above,

$$E_{\alpha\gamma} = \frac{\mathbf{u}_\alpha \cdot \mathbf{u}_\gamma}{r^3} - \frac{3(\mathbf{u}_\alpha \cdot \mathbf{r})(\mathbf{u}_\gamma \cdot \mathbf{r})}{r^5},$$

which is just the interaction energy of the permanent dipoles. $\exp(-E_{\alpha\gamma}/kT)$ can be approximated by $1 - E_{\alpha\gamma}/kT$; the next significant contribution to $\mathbf{F}_{(3)}$ comes from the term in $(E_{\alpha\gamma}/kT)^3$, which is of the order of $(1/3!)(1/5)^2$ of the term retained.

Finally, let the position of P be given by spherical polar coordinates with origin O and pole $\mathbf{k}(r, \theta_1, \varphi_1)$; the orientation of γ , by the Eulerian coordinates $(\theta_2, \varphi_2, \psi_2)$ of a set of axes (i' , j' , k') fixed in γ , center P , \mathbf{k}' along \mathbf{u}_γ . ψ_2 integrates out at once and we get $(d_{\alpha\gamma} = r_\alpha + r_\gamma = \text{sum of radii of spheres})$

⁴⁴ It is proposed to examine these in subsequent papers.

⁴⁵ P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929), pp. 30–32.

$$\begin{aligned} \mathbf{F}_{(3)} &= \frac{N_\gamma}{4\pi V} \int_{d_{\alpha\gamma}}^\infty r^2 dr \int_0^\pi \sin \theta_1 d\theta_1 \int_0^{2\pi} d\varphi_1 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^{2\pi} d\varphi_2 \cdot \left[1 - \frac{E_{\alpha\gamma}}{kT} \right] \cdot \mathbf{F}_\gamma \\ &= \frac{N_\gamma}{4\pi V} \int_{d_{\alpha\gamma}}^\infty r^2 dr \int d\Omega_1 d\Omega_2 \left[1 - \frac{1}{kT} \left(\frac{\mathbf{u}_\alpha \cdot \mathbf{u}_\gamma}{r^3} - \frac{3(\mathbf{u}_\alpha \cdot \mathbf{r})(\mathbf{u}_\gamma \cdot \mathbf{r})}{r^5} \right) \right] \left[-\frac{\mathbf{u}_\gamma}{r^3} + \frac{C\mathbf{u}_\alpha}{r^6} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\gamma)}{r^5} + \frac{3C\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\alpha)}{r^8} \right]. \end{aligned} \quad (40)$$

Introducing the coordinates $(r, \theta_1, \varphi_1, \theta_2, \varphi_2)$ and performing the indicated operations, we get

$$F_{(3)1} = 0; \quad F_{(3)2} = 0; \quad F_{(3)3} = \frac{2}{d_{\alpha\gamma}^3} \cdot \mu_\alpha \cdot \frac{N_\gamma}{V} \cdot \frac{4\pi}{3} \left[C + \frac{\mu_\gamma^2}{3kT} \right]. \quad (41)$$

We may now complete the calculations of $(F_\delta)_{av}$ undertaken in Section 6. From Eqs. (31) and (41), (Case I, for imperfect gases), letting $n_\alpha = N_\alpha/V$, $n_\beta = N_\beta/V$, $n_\gamma = N_\gamma/V$.

$$[F_\delta]_{av} = (3\delta) \left\{ \frac{2\mu_\alpha}{d_{\alpha\alpha}^3} \cdot \frac{4\pi}{3} \cdot n_\alpha \left[A + \frac{\mu_\alpha^2}{3kT} \right] + \frac{2\mu_\alpha}{d_{\alpha\beta}^3} \cdot \frac{4\pi}{3} \cdot n_\beta \left[B + \frac{\mu_\beta^2}{3kT} \right] + \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{4\pi}{3} \cdot n_\gamma \left[C + \frac{\mu_\gamma^2}{3kT} \right] \right\}. \quad (42)$$

Supposing $d_{\alpha\alpha}$, $d_{\alpha\beta}$, $d_{\alpha\gamma}$ are all nearly equal, we obtain by using the Debye relationship and the law of mixtures,

$$[F_\delta]_{av} = (\delta/3) \cdot (2\mu_\alpha/d^3) \cdot ((\epsilon - 1)/(\epsilon + 2)), \quad (43)$$

where ϵ is the dielectric constant of the gas.⁴⁶

This equation is almost identical with (28), which was derived from an entirely different point of view. The relationships (43) hold only for molecules with a single (or zero) dipole moment: they do not hold for other types of molecules. These will show a different relation between $[F_\delta]_{av}$ and the dipole moments and polarizability of the solvent molecules and therefore, in general, no simple relation with ϵ .

From Eqs. (38) and (41), (Case II, for dilute solutions)

$$[F_\delta]_{av} = g_{(\gamma)\delta}(N_\beta) + \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{4\pi}{3} \cdot n_\gamma \left[C + \frac{\mu_\gamma^2}{3kT} \right] (3\delta), \quad (44)$$

$$[F_\delta]_{av} = g_{(\gamma)\delta}(N_\beta) + \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{n_\gamma}{N} P_\gamma (3\delta) \quad N = 6.06 \times 10^{23}$$

$$\text{introducing} \quad P_\gamma = \frac{4\pi}{3} N \left[C + \frac{\mu_\gamma^2}{3kT} \right],$$

the molar polarization.⁴⁶

In general, P_γ is a function of the concentration; its variation may be considered to be due to the association of the γ -molecules.⁴⁷ Provided

⁴⁶ P. Debye, reference 45, Chap. II, III.

⁴⁷ C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Co., New York, 1929), Chap. IX.

the associated molecules satisfy the conditions as to the type of the γ -molecules (assumption *i*), P_γ will continue to be a measure of the field acting on a dipole and Eq. (44) will hold for concentrations where P_γ differs markedly from $(4\pi/3)N[C + (\mu_\gamma^2/3kT)]$. Experimentally, it is found that (44) remains valid throughout the entire concentration range (Section 7). Eq. (44) holds therefore for monodipolar solute molecules which exhibit association of the type $\begin{smallmatrix} -+ \\ \rightleftharpoons \\ +- \end{smallmatrix}$ (zero moment) that is, for the most common type of association. It will not hold for molecules which associate chain-wise, or in fact for other types of association giving a zero moment unless the dipoles are so close that the cancelation of field is complete at small distances.

We have, taking only one substance to be optically active

$$\alpha = \frac{\pi}{\lambda_{vac.}} \cdot \frac{n^2 + 2}{3} \cdot \frac{n_\alpha}{6} \{ \sigma'_{\xi\eta\zeta}(0) + \sigma'_{\xi\eta\zeta} [F_\delta]_{av} \} [\xi\eta\zeta], \quad (24')$$

which may be put in the form

$$[\alpha]/(n^2 + 2) \equiv \Omega = \Omega_1 + \Omega^3 [F_\delta]_{av}. \quad (45)$$

Then, from (43) and (45)

$$\Omega = \Omega_1 + \Omega^3 \cdot (2\mu_\alpha/d^3) \cdot ((\epsilon - 1)/(\epsilon + 2)) \quad (46)$$

and from (44) and (45)

$$\Omega = \Omega_1 + \Omega^3 g_{(\gamma)\delta}(N_\beta) + \Omega^3 \cdot \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{n_\gamma}{N} \cdot P_\gamma. \quad (47)$$

SECTION 7

The experimental manifestations of the equations found in Section 6 divide themselves naturally into two parts: the gross effects observed on changing the solvent radically, that is, replacing one solvent by another, and the detailed effects which result from modifying the solvent by degrees by the introduction of increasing quantities of a third substance. For the first of these, Eq. (46), although derived for imperfect gases, will hold to a crude approximation for liquids, and will serve to illustrate the general trend. For the detailed effects, Eq. (47) must be used.

Part I. Gross effects

The fundamental equation here is

$$\Omega = \Omega_1 + \Omega^3 \cdot \frac{2\mu_\alpha}{d^3} \cdot \frac{\epsilon - 1}{\epsilon + 2} = \Omega_1 + \Omega^3 \cdot \frac{2\mu_\alpha}{d^3} \left\{ B + \frac{\mu_\beta^2}{3kT} \right\}, \quad (48)$$

taking $N_\gamma = 0$, and N_α/N_β small.

A. The dependence of the rotatory power on ϵ .—P. Walden,³⁸ reviewing the experimental data up to 1905, concluded that the sequence of solvents arranged in order of their effect on rotatory power, was practically identical with the sequence arranged in order of dielectric constant. In a more recent series of investigations, H. G. Rule,⁴⁸ has attempted to correlate the rotation of a compound in a series of related solvents with the dipole moment of the solvent molecules. From (43), we see that, if $\mu_\beta \neq 0$ so that we can neglect B , there will be a rough relation between rotation⁴⁹ and dipole moment. For $\mu_\beta = 0$, Rule's curve⁴⁸ becomes multiple valued, a circumstance which indicates that μ_β is not the sole factor in the variations of rotation. This factor is, according to Eq. (48), the polarizability of the solvent. Figs. 2, 3, and 4 give plots of the rotivity Ω against r , the dielectric ratio $(\epsilon - 1)/(\epsilon + 2)$. The points are distributed about a straight line, as predicted, and the multiple value is removed.

B. The dependence on dipole moment of solute.—Wolf and Volkmann,²⁰ in an attempted verifica-

tion of the Born-Gans rule (Section 1), conclude that the relation

$$\text{Rotivity} = \Omega = \text{Constant}$$

holds sufficiently well for active compounds with small dipole moments, but not at all for substances like 1-menthone, whose moment is 2.83 debyes. From our point of view, this shows that if $\mu_\alpha = 0$, the second term of (48) vanishes.

Our general set-up indicates that a molecule with no moment will create no external field: in particular, by Eq. (48), the plot of Ω against r must be a straight line of zero slope. This is strikingly confirmed for *d*-pinane.⁵⁰ (Fig. 5; contrast Fig. 3.)

We notice in passing that *d*-pinane is the best example yet found of the superiority of the rotivity over the rotation as a measure of optical rotatory power. There is a decided drift of rotation with refractive index of solvent, but none at all for the rotivity.

C. The separation of solvents into classes.—The experimental data indicates some very important differences in the behavior of solvents which can be interpreted in the light of our theory. First, it is found that aromatic and aliphatic solvents must be treated separately (Figs. 2 and 3). Within each of these classes of solvents the agreement with theory is good. Their different behavior will be discussed more fully later (Section 7, Part II, *D*). Secondly, we find that the points for the compounds CCl_4 , CHCl_3 , CHBr_3 , and CS_2 all fall below the line for aliphatic solvents generally, indicating that the field of these compounds is greater than that given by $(2\mu_\alpha/d^3)((\epsilon - 1)/(\epsilon + 2))$. The fundamental physical reason behind this is that the field measured by the change in rotivity $\Delta\Omega$ and the polarization measured by the dielectric constant reflect, respectively, the effects of an electric dipole at short range and at long range. These effects do not necessarily coincide. This may be illustrated most easily in the case of CS_2 . The CS_2 molecule is linear, with the two $\text{C} \rightarrow \text{S}$ dipoles oriented opposite to one another. If we consider one dipole localized at a point 1 and the other at a point 2, then the dipole field of the molecule at some point P is given by

⁴⁸ H. G. Rule, *Studies in Solvent Action*. I, J. Chem. Soc. 674 (1931); II, *ibid.* 2652 (1931); III, 1400 (1932); IV, 1409 (1932); V, 2332 (1932); VI, 376 (1933); VII, 1217 (1933).

⁴⁹ In discussing the data of other workers we will occasionally use the rotation instead of the rotivity.

⁵⁰ H. G. Rule and A. R. Chambers, *Nature* 133, 910 (1934).

TABLE I. *1-Menthyl methyl naphthalate in aromatic solvents**
($c = 4$).⁴⁸

Solvent	$-[M]^{20}_{5461}$	$-M\Omega^{20}_{5461}$	r
Benzene	543	127	.302
Mesitylene	583	137	.311
Toluene	546	129	.315
Anisole	466	108	.528
Iodobenzene	465	100	.546
<i>o</i> -Chlorotoluene	502	116	.554
Brombenzene	466	104	.595
<i>m</i> -Chlorotoluene	497	115	.603
Chlorbenzene	463	107	.606
<i>p</i> -Chlorotoluene	433	101	.634
Aniline	443	98	.656
<i>o</i> -Dichlorbenzene	433	98	.746
Acetophenone	454	104	.845
Benzaldehyde	432	98	.846
Benzonitrile	372	85	.890
Nitrobenzene	423	96	.917

* The rotivity was calculated using the values for n for the pure solvent taken from the I.C.T.; the dielectric constants were taken from the same source or from A. Weissberger and E. Proskauer, *Organic Solvents* (Clarendon Press, Oxford, 1935), if listed there.

$$((\mathbf{p} \cdot \mathbf{r}_{1P})/r_{1P}^3) - ((\mathbf{p} \cdot \mathbf{r}_{2P})/r_{2P}^3),$$

where \mathbf{p} is the moment of one C→S bond, r_{1P} and r_{2P} are the distances from points 1 and 2 to P , respectively. At great distances where $\mathbf{r}_{1P} = \mathbf{r}_{2P}$, the field vanishes. Such is the case for the interaction of this field with an external field like that existing between condenser plates. At short distances, however, where the effect of the dipoles on the rotivity is greatest, the field does *not* vanish and the molecule CS_2 acts strongly polar. This will be true of all molecules with more than one dipole.

To find the equation corresponding to (43) for these molecules, we merely have to make a different assumption (*i*), substitute in (39) and perform the indicated operations.⁴⁴

So far we have neglected the effect of group size and "screening" by our tacit assumption $d = \text{constant}$. There is no necessity for doing this, and obviously an increase of size of the dipole carrier will be reflected by an increase in d and a corresponding decrease in field. This, as well as the comparative effects of *o*, *m*, and *p*-substituents, has been discussed experimentally by Rule.⁴⁸ his conclusions fit unchanged into the above theory.

D. The temperature effect.—As T increases, the term $\mu_\beta^2/3kT$ in (48) decreases, and the effect of the dipole moment of the solvent diminishes. Hence, for increasing temperatures the values of

the rotations in polar solvents must converge towards the values in nonpolar solvents. Data supporting this conclusion are listed by Lowry.⁵¹

Part II. Detailed effects

From (47), denoting by the superscript ⁰ the values of the quantities concerned when $N_\gamma = 0$, we obtain

$$\Omega - \Omega^0 = \Omega^0 [g_{(\gamma)\delta}(N_\beta) - g_{(\gamma)\delta}(N_\beta^0)] + \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{\Omega^0}{N} \cdot \frac{n_\gamma}{N} \cdot P_\gamma.$$

Setting

$$G(\beta, \gamma) = (\Omega^0/n_\gamma) \{g_{(\gamma)\delta}(N_\beta) - g_{(\gamma)\delta}(N_\beta^0)\} N,$$

$$K_\gamma = (2\mu_\alpha/d_{\alpha\gamma}^3) \Omega^0 \quad \text{and} \quad n_\gamma/N = w_\gamma/50M_\gamma,$$

where w_γ is the weight of substance γ in a solution made up to 50 cc. (see Section 8), and M_γ , the molecular weight of γ , we get

$$\Omega - \Omega^0 = \frac{w_\gamma}{50M_\gamma} G(\beta, \gamma) + \frac{w_\gamma}{50M_\gamma} K_\gamma P_\gamma, \quad (49)$$

$$S \equiv \frac{\Omega - \Omega^0}{w_\gamma} \cdot 50M_\gamma = G(\beta, \gamma) + K_\gamma P_\gamma. \quad (50)$$

Since $g_{(\gamma)\delta}(N_\beta)$ is smoothly varying (that is, dg/dw_γ varies slowly), $G(\beta, \gamma)$ is constant or nearly so. If P_γ changes decidedly, the variations

TABLE II. *1-Menthyl methyl naphthalate in aliphatic solvents*
($c = 4$).⁴⁸

Solvent	$-[M]^{20}_{5461}$	$M\Omega^{20}_{5461}$	r
<i>n</i> -Pentane	651	169	.220
<i>n</i> -Hexane	653	167	.233
<i>n</i> -Heptane	653	166	.244
Cyclo-Hexane	688	170	.252
Ethyl ether	495	129	.537
Acetic acid	423	108	.631
Methyl Iodide	336	77	.670
Ethyl iodide	383	88	.681
Ethyl bromide	360	89	.823
Nitroethane	282	71	.862
Acetaldehyde	336	83	.873
Methyl cyanide	239	63	.924
Nitromethane	219	56	.924
Tetranitromethane	651	160	.274
Carbon tetrachloride	563	136	.289
Carbon disulfide	437	93	.358
Chloroform	362	88	.548
Bromoform	429	94	.554
Dichloromethane	267	66	.803

⁵¹ T. M. Lowry, *Optical Rotatory Power*, pp. 354–356.

TABLE III. 1-Menthyl *o*-nitrobenzoate in aromatic solvents ($c=4$).*

Solvent	$-[M]_{5461}^{20}$	$-M\Omega_{5461}^{20}$	r
Benzene	713.8	166.8	.302
Toluene	671.0	157.9	.315
Anisole	603.3	139.7	.528
Brombenzene	580.4	130.0	.595
Benzaldehyde	500.1	113.6	.846
Phenyl cyanide	465.1	106.4	.890
Nitrobenzene	422.7	95.3	.917

* A. McLean, J. Chem. Soc. 352 (1934).

in $G(\beta, \gamma)$ will be negligible: we may, therefore, take G to be a constant.

For experimental verification of Eqs. (49) and (50) none of the data in the literature is adequate. The experiments described immediately below were performed for this purpose.

A. S is a linear function of P_γ .—The first and most fundamental relationship which is subject to experimental verification is Eq. (50) which predicts that S is a linear function of P_γ .⁵² Tables V, VI, VII and VII give the observed data, and Figs. 6, 7, 8 and 9 are plots of S against P_γ for a number of systems. The agreement is within the experimental error for all points; the equation holding even for solutions containing pure dipole solvent.

If Ω and P_γ both varied smoothly with the concentration of added polar compound, the observed linearity might be considered fortuitous. This is not the case. For the system diacetyl diethyl *d*-tartrate—benzene—nitrobenzene, Ω exhibits the surprising property of rising to a maximum at 5 grams of nitrobenzene (Fig. 10, middle curve) and then falling off rapidly with the further addition of nitrobenzene to a final value *below* the initial. At the same time, P_γ changes from about 360 cc at 0 grams of nitrobenzene to 94 cc at 0 grams of benzene, the slope of the polarization-concentration curve changing from a large negative value to almost zero (Fig. 10, inset). In spite of this, the graph of S against P_γ (Fig. 6) is a straight line. Similar considerations hold for diacetyl diethyl *d*-tartrate—benzene—chlorobenzene; diacetyl diethyl *d*-tartrate—benzene—benzonitrile; and *d*-limonene

⁵² Note that Rule's M_2 , aside from the factor $(n^2 + 2)^{-1}$, is related to S by factors depending on the concentrations alone. Hence, the observed "parallelism" between M_2 and P_γ is here predicted.

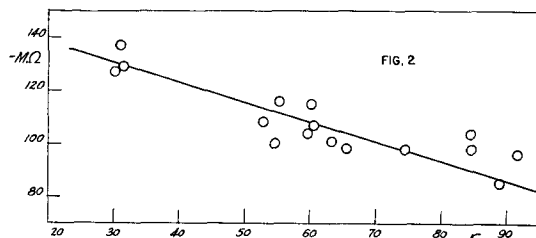


FIG. 2

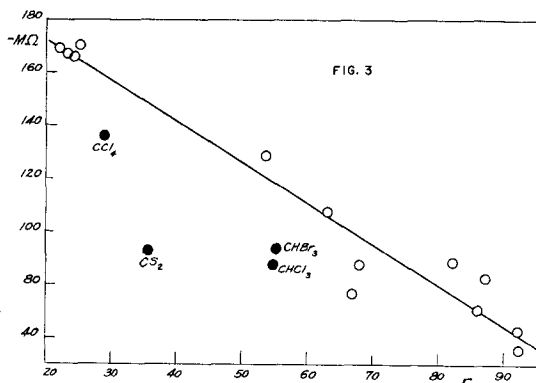
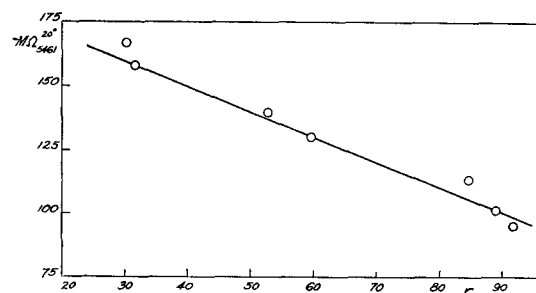


FIG. 3

FIG. 2. 1-Methyl methyl naphthalate in aromatic solvents.
FIG. 3. 1-Methyl methyl naphthalate in aliphatic solvents.

FIG. 4. 1-Menthyl *o*-nitrobenzoate in aromatic solvents.

—benzene—nitrobenzene (Figs. 11, 7, 8 and 9). The inference is inescapable that we are here dealing with a relationship of cause and effect.

It is evident from the derivation that $G(\beta, \gamma)$ and K_γ must be of opposite sign, since the former represents a decrease in the field while the latter represents an increase. Thus for a compound for which P_γ decreases markedly, we would expect to find S sometimes of one sign and sometimes of the other, depending on whether $|K_\gamma P_\gamma|$ or $|G(\beta, \gamma)|$ is the greater quantity. This is actually the case for diacetyl diethyl tartrate—benzene—nitrobenzene (Table V). Conversely, for solutions for which P_γ is fairly constant, we expect S to be relatively stationary: this is shown by diacetyl

diethyl tartrate—benzene—chlorbenzene (Table VI).

The excellent linearity of the relation between S and P_γ confirms the validity of Eq. (22), and also the deduction that $G(\beta, \gamma)$ is a constant; for without both of these being true, the observed strict linearity could not occur.

B. The variation of Ω with w_γ .—Returning to Eq. (49) and differentiating, we obtain

$$50M_\gamma(d\Omega/dw_\gamma) = G(\beta, \gamma) + K_\gamma P_\gamma + K_\gamma w_\gamma(dP_\gamma/dw_\gamma) \\ = S + K_\gamma w_\gamma(dP_\gamma/dw_\gamma).$$

We see the possibility of a change of sign of $d\Omega/dw_\gamma$ if dP_γ/dw_γ is large and negative. This change of sign is actually observed when nitrobenzene is used as the polar (γ) solute. (Table V; this also holds for 1-menthyl methyl naphthalate⁴⁸.)

Figs. 10 and 11 show how the various differently shaped curves for Ω against w_γ result from the curves for $w_\gamma P_\gamma$ and $w_\gamma G(\beta, \gamma)$ against w_γ , by means of Eq. (49)

$$\Omega - \Omega^0 = \frac{w_\gamma G(\beta, \gamma)}{50M_\gamma} + \frac{K_\gamma w_\gamma P_\gamma}{50M_\gamma}. \quad (49')$$

The values of $G(\beta, \gamma)$ and K_γ are taken from Figs. 6 and 7; the experimental values of $w_\gamma P_\gamma$, multiplied into $K_\gamma/50M_\gamma$ are plotted as ordinates, and $(w_\gamma/50M_\gamma)G(\beta, \gamma)$ is added to it: the curves for $\Omega - \Omega^0$ are deduced. The steep initial slope of the $P_\gamma - w_\gamma$ curve for nitrobenzene (Fig. 10) and its rapid falling off, result in a maximum for $\Omega - \Omega^0$; the corresponding $P_\gamma - w_\gamma$ curve for benzonitrile, because of the smaller value of

TABLE IV. *d*-Pinane⁵⁰ ($c = 3.5$).

Solvent	$[\alpha]_D$	η_D	Ω_D	r
Methanol	19.3	1.3312	5.12	.910
Acetaldehyde	20.1	1.3316	5.30	.873
Acetonitrile	19.3	1.3460	5.05	.924
Acetone	20.9	1.3589	5.39	.872
Acetic acid	19.5	1.3715	5.00	.631
<i>n</i> -Hexane	20.1	1.3760	5.15	.233
Nitromethane	19.8	1.3813	5.05	.924
<i>n</i> -Heptane	21.1	1.3867	5.38	.244
Methylene chloride	21.0	1.4237	5.19	.803
Chloroform	21.8	1.4464	5.32	.548
Carbon tetrachloride	22.9	1.4607	5.52	.289
Methyl iodide	23.6	1.5293	5.44	.670
Carbon disulfide	28.1	1.6204	5.99	.358
Methylene iodide	26.6	1.7559	5.22	.600

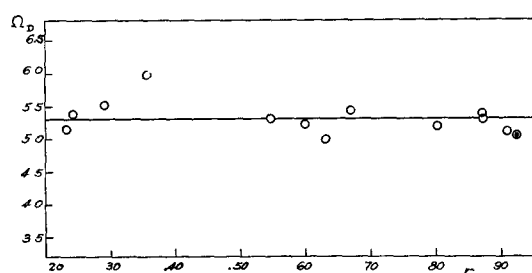


FIG. 5. *d*-Pinane.

$G(\beta, \gamma)$, gives only a flattening of the Ω -curve (Fig. 11).

In Tables IX and X, $\Omega - \Omega^0$ calculated from the right-hand side of (49) is compared with the measured value. The average deviations are, respectively, 0.013° and 0.018° , which is roughly the probable error of the experimental values. It will be noticed that it is possible to predict the rotivities from measurements of the dielectric constant more accurately than they can be read with the polariscope and refractometer.

The slope of the $\Omega - w_\gamma$ curve at the origin is given by

$$G(\beta, \gamma) + K_\gamma P_\gamma.$$

Depending on the relative magnitudes of the two terms, this slope may be positive or negative. Thus *d*-camphor shows a negative slope for benzene-chlorbenzene and a positive slope for benzene-nitrobenzene.

For *d*-limonene, the slopes for both chlorbenzene and nitrobenzene are positive, with the latter greater; for diacetyl diethyl *d*-tartrate, both slopes are again positive, but now the slope for chlorbenzene is greater (Tables V, VI, VIII, XII). All these apparently contradictory results take a natural position in the description here given.

C. The conditions on P_γ .—Højendahl⁵³ has shown that nitrobenzene associates to give a complex of zero moment. Therefore, the observed confirmation of Eq. (50), which holds only if the complexes have zero moment, is to be expected.

An analysis of the $P_\gamma - w_\gamma$ curve for ethanol in cyclohexane (compare Table XIII) leads to the conclusion that at low alcohol concentrations ethanol exhibits chain-wise association, and that at higher concentrations the chains break up so

⁵³ K. Højendahl, Thesis, Copenhagen, 1928.

TABLE V. *Diacetyl diethyl d-tartrate—benzene—nitrobenzene.**

w_α	w_β	w_γ	—Rotation $^{25}_{5461}$ (2 dm)	n^{25}_{5461}	r	Ω^{25}_{5461}	S	P_γ
4.994	39.893	00.000	2.890	1.49495	.3393	3.416
5.007	39.81	00.000	2.865	1.49389	...	3.380
5.007	39.78	00.000	2.897	1.49389	.3389	3.418
5.003	39.827	00.000	2.884	1.49424	.3391	3.405 (mean)
5.003	38.91	1.197	2.840	1.49485	.3941	3.351	278	314.9
4.999	38.096	2.469	2.827	1.49732	.4437	3.333	179	290.2
5.001	38.03	2.472	2.800	1.49590	.4433	3.303	254	289.9
5.005	37.22	3.587	2.755	1.49703	.4814	3.245	274	274.8
4.999	36.450	4.744	2.782	1.49941	.5156	3.275	169	258.9
5.008	36.30	4.824	2.775	1.49837	.5182	3.263	181	259.0
5.000	35.48	5.975	2.785	1.49932	.5486	3.278	131	246.3
5.013	35.520	5.996	2.782	1.50044	.5492	3.263	146	245.6
4.995	34.599	7.349	2.802	1.50177	.5810	3.296	91	232.5
4.999	32.951	9.573	2.847	1.50384	.6248	3.341	41.1	213.8
4.997	31.170	12.008	2.892	1.50598	.6656	3.390	7.7	197.6
5.007	29.451	14.383	2.984	1.50813	.6979	3.486	— 34.7	183.7
5.005	27.684	16.788	3.074	1.51034	.7259	3.587	— 66.7	172.1
5.019	26.805	17.998	3.118	1.51117	.7390	3.626	— 75.6	167.0
5.005	22.415	24.004	3.410	1.51712	.7884	3.960	—142	145.6
5.010	18.108	29.975	3.736	1.52225	.8254	4.319	—188	130.2
5.007	00.000	54.77	5.210	1.54501	.9085	5.930	—284	94.46

* The subscript α refers to the first substance mentioned in the title, β the next, and γ the next. Thus, here w_α is weight of diacetyl diethyl tartrate, w_β that of benzene, w_γ that of nitrobenzene.

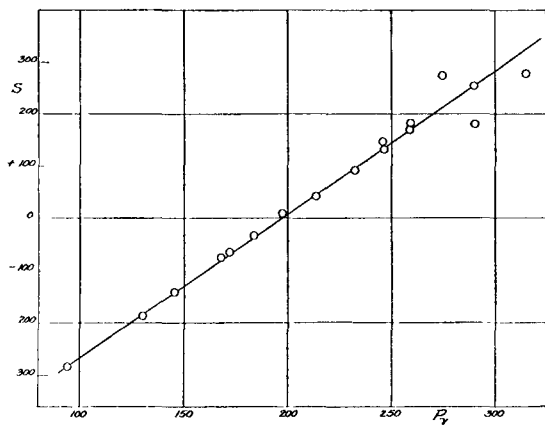
TABLE VI. *Diacetyl diethyl d-tartrate—benzene—chlorobenzene.*

w_α	w_β	w_γ	—Rotation $^{25}_{5461}$ (2 dm)	n^{25}_{5461}	r	— Ω^{25}_{5461}	S	P_γ
5.003	39.827	00.00	2.884	1.49424	.3391	3.405
5.007	37.62	2.743	2.770	1.49504	.3620	3.266	285	77.72
5.003	35.430	5.520	2.667	1.49618	.3840	3.145	265	76.22
5.008	33.23	8.308	2.562	1.49798	.4045	3.014	265	74.68
5.005	31.074	11.030	2.472	1.49912	.4234	2.907	254	73.38
5.006	28.89	13.802	2.335	1.50035	.4410	2.744	269	71.89
5.006	26.686	16.551	2.292	1.50158	.4550	2.689	243	69.81
5.009	22.352	22.072	2.135	1.50421	.4892	2.500	231	68.61
5.007	18.010	27.539	2.010	1.50683	.5168	2.350	216	66.67
5.007	13.669	33.042	1.900	1.50933	.5432	2.218	202	65.10
5.006	00.000	50.31	1.660	1.51748	.6090	1.927	165	60.53

TABLE VII. *Diacetyl diethyl tartrate—benzene—benzonitrile.*

w_α	w_β	w_γ	—Rotation $^{25}_{5461}$	n^{25}_{5461}	r	— Ω^{25}_{5461}	S	P_γ
5.007	39.822	00.000	2.897	1.49389	.3418	3.418	.	.
5.006	35.464	5.023	2.550	1.49723	.5468	3.002	427	243.5
5.006	34.590	6.019	2.468	1.49780	.5471	2.905	419*	231.6
5.005	32.838	8.046	2.411	1.49913	.6210	2.835	359*	211.1
5.006	31.097	10.047	2.375	1.50035	.6583	2.790	322	194.2
5.005	28.927	12.549	2.311	1.50196	.6962	2.712	280*	177.2
5.007	26.750	15.062	2.275	1.50346	.7270	2.666	257	163.2
5.006	22.363	20.092	2.230	1.50655	.7721	2.608	208	141.6
5.006	13.648	30.107	2.151	1.51264	.8302	2.505	156	114.6
5.005	00.000	45.760	2.032	1.52243	.8795	2.351	120	91.43

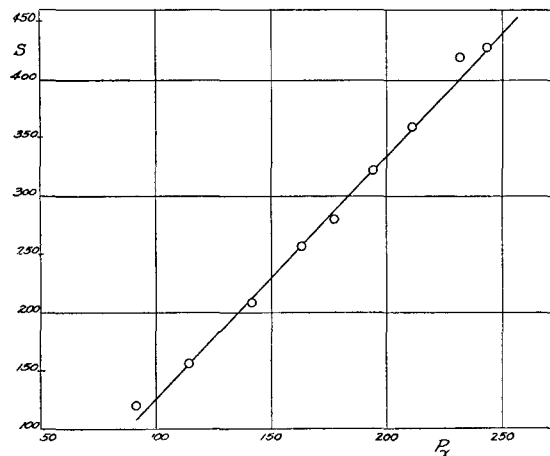
* For these points $\Omega^0 = 3.395$.

FIG. 6. Diacetyl diethyl *d*-tartrate in benzene-nitrobenzene mixtures.

that the dielectric properties of alcohol approach once more those of a normal liquid.⁴⁷

Accordingly, we expect that S will *not* be linear in P_γ . The $S-P_\gamma$ curve for *d*-camphor—cyclohexane—ethanol (Fig. 12) demonstrates that alcohol does not associate in the normal fashion. We distinguish three distinct sections of the curve. The first, (*AB*), corresponding to the initial decrease in P_γ ; the second, (*BC*), corresponding to the rise of P_γ ; and the third, (*CD*), corresponding to the breaking down of the alcohol chains and the return to normal behavior of the solution. In this last portion of the $S-P_\gamma$ curve, we see, indeed, that the rate of change of slope is vanishing and we are returning once more to the linear law $S=G(\beta, \gamma)+K_\gamma P_\gamma$.

The data just given represent independent

FIG. 7. Diacetyl diethyl *d*-tartrate in benzene-benzonitrile mixtures.

evidence concerning the nature of alcohol complexes in solution: it confirms the conclusions of Smyth.⁴⁷

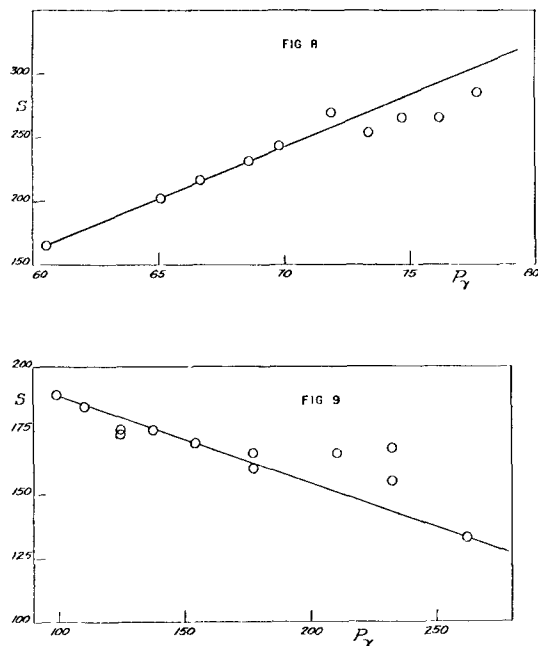
D. The influence of the benzenoid nucleus. For aromatic compounds assumption (*i*) Section 6, is obviously inadequate. The present state of our knowledge concerning the short-range field of a benzenoid ring, although indicating a very large one,⁵⁴ is nevertheless not enough to present us with a satisfactory substitute for (*i*). But for our present purpose, which is to correlate changes in rotivity with that part of the solvent field caused by dipoles, such detailed information is not necessary. To be able to eliminate the effect of benzene rings, it is sufficient to establish that

TABLE VIII. *d*-Limonene—benzene—nitrobenzene.

w_α	w_β	w_γ	Rotation] ²⁵ ₅₄₆₁	n_{5461}^{25}	r	Ω_{5461}^{25}	S	P_γ
4.178	39.229	00.000	23.935	1.49780	.3013	33.751
4.1844	39.228	00.000	23.970*	1.49768	...	33.751
4.179	37.059	3.051	24.008	1.50054	.4352	33.781	61	299.9
4.179	34.912	5.981	24.125	1.50328	.5268	33.880	133	262.3
4.1826	32.717	9.0305	24.268*	1.50627	...	33.979	155	...
4.179	32.710	9.040	24.260	1.50627	.5987	33.998	168	232.6
4.181	30.552	11.993	24.380	1.50914	.6526	34.080	166	210.6
4.1850	26.308	17.881	24.609*	1.51466	...	34.234	166	...
4.179	26.260	17.963	24.563	1.51475	.7301	34.217	160	177.2
4.178	21.891	23.973	24.795	1.52037	.7839	34.412	170	154.2
4.171	17.557	29.923	24.985	1.52570	.8223	34.603	175	137.5
4.1852	13.227	35.865	25.294*	1.53139	...	34.772	175	...
4.179	13.205	35.903	25.250	1.53148	.8516	34.761	173	124.7
4.179	6.619	44.900	25.645	1.54006	.8839	35.092	184	110.3
4.178	0.000	54.031	26.025	1.54833	.9075	35.414	189	99.49

* These rotations have been corrected for racemization.

⁵⁴ G. Briegleb, Zeits. f. physik. Chemie **B31**, 58 (1935).

FIG. 8. Diethyl diacetyl *d*-tartrate in benzene-chlorobenzene mixtures.FIG. 9. *d*-Limonene in benzene-nitrobenzene mixtures.

the field of the benzene-nuclei varies smoothly with concentration.

This result, indeed, has already been shown indirectly, since $G(\beta, \gamma)$ could not be constant if this proposition were not true. The experiments of gradually replacing cyclohexane as solvent by benzene or diphenyl (Tables XIV and XV; Fig. 13) demonstrate it directly.

We note that the effect of the phenyl groups of benzene and of diphenyl is almost the same in spite of the difference in geometrical structure of the molecules (Fig. 13). Finally we remark that in the experiments actually performed, replacing benzene by benzene derivatives as solvent (Part II, A), the change in the number of benzene groups corresponds to only the last seventh of the range of this last experiment. Over this region we can even say that the field of the benzene-nuclei varies *linearly* with the concentration.

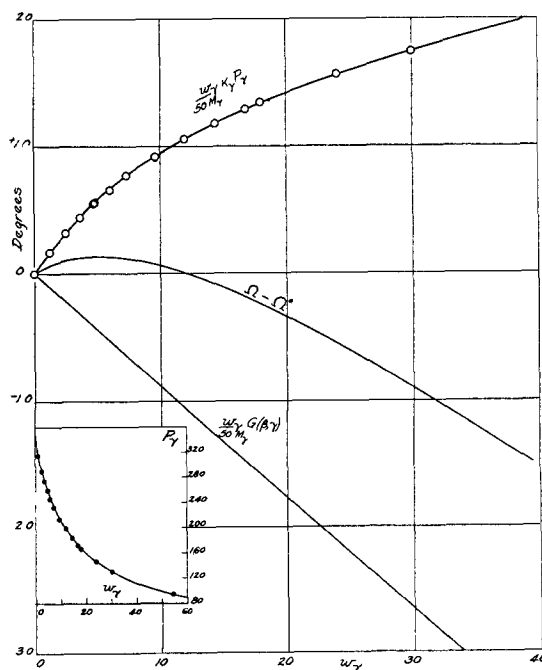
E. Conclusions concerning the active molecule.—Unusual interest attaches to studies of tartaric acid and derivatives, partly on historical grounds, partly because of their remarkable properties.⁵⁵

⁵⁵ T. M. Lowry, reference 51, Chap. 23.

Diacetyl diethyl *d*-tartrate is typical of these compounds. Table XVI gives the specific rotation of this compound in different solvents.

From our viewpoint, it seems likely that the "anomalous" behavior of optically active compounds has been considerably overestimated: it was therefore of particular importance to show that this chemically very stable compound acts normally. Tables V, VI and VII (Figs. 6, 7 and 8) show that there is not the slightest irregularity in the reactions of diacetyl diethyl tartrate to its solvents. We have already shown (Section 7, Part II, B) that change of sign of rotation may occur through simple deformation. A comparison of Tables V and VIII makes clear that there is a difference neither in kind nor in degree between the reactions of *d*-limonene and diacetyl diethyl *d*-tartrate.

The properties of the active molecule enter by way of the quantity $K_\gamma = (2\mu_\alpha/d_{\alpha\gamma}^3)\Omega^3$. If K_γ is to have any physical significance, it is an elementary requirement that it should be not far different for two compounds as much alike as nitrobenzene and benzonitrile. We find (Tables IX and X) the values are, respectively, 2.705 and 2.098

FIG. 10. Diacetyl diethyl *d*-tartrate in benzene-nitrobenzene mixtures.

(with diacetyl diethyl tartrate), corresponding to

$$\frac{d_{\alpha\gamma}(\text{benzonitrile})}{d_{\alpha\gamma}(\text{nitrobenzene})} = 1.088.$$

The value of K_γ for limonene with nitrobenzene, (0.336), (Table VIII), is much smaller than that for diacetyl diethyl tartrate with nitrobenzene (2.705). If we attribute this difference to the different values of μ_α , we obtain the result that *d*-limonene has a dipole moment of about 0.3 debye (taking the μ of diacetyl diethyl tartrate as 3 debyes). This agrees with the value of 0–0.5 debyes found by Wolf and Volkmann.²⁰ In any case, we must conclude from the very existence of the K_γ that *d*-limonene has a moment.

F. Concentration effect.—It is plain that a change of the concentration of active stuff is equivalent to a change in N_γ , and the concentration effect is therefore a special case of the general solvent effect.

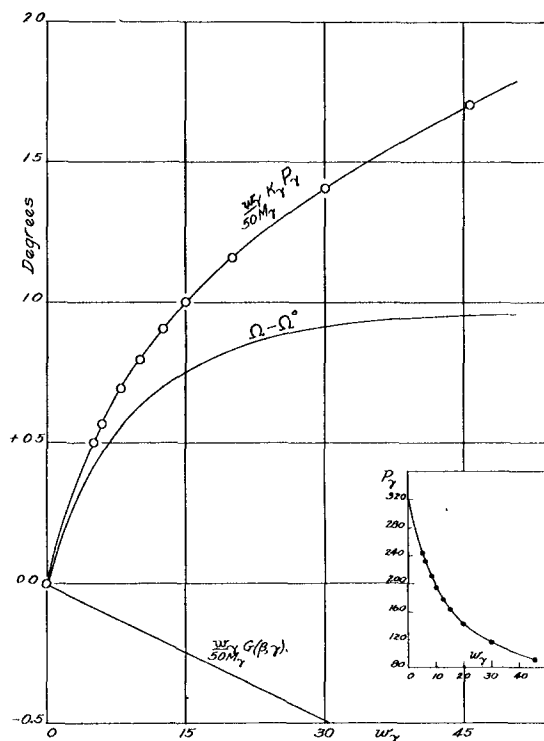


FIG. 11. Diacetyl diethyl *d*-tartrate in benzene-benzonitrile mixtures.

SECTION 8

I. Design of experiments. Calculations

The large amount of data on optical rotatory power in various solvents cannot be used for our purpose because of the lack of the two other relevant pieces of information: index of refraction n , and dielectric constant ϵ . That the refractive index of the solution whose rotation is measured, is a significant quantity, has been known since 1915;¹⁴ nevertheless, Wolf and Volkmann²⁰ are the only two investigators who have used it systemically. That ϵ is significant, we believe to be shown in this paper, if not by the previous qualitative work of Rule.⁴⁸ The experiments described below contain the first simultaneous measurements of dielectric constant, refractive index and rotation.

The choice of solvents is an extremely important factor: an arbitrary and random selection has too often resulted in a hopeless confusion. For our purpose it was essential to choose closely related compounds, whose sole differences were in the magnitude of dipole moment. These conditions were satisfied by the monosubstituted aromatic compounds. It was further necessary to choose compounds with large and variable P_γ . The experimental conditions of stability, nonconductivity, high boiling point, and purity, reduced the number of available compounds to four: benzene, chlorobenzene, benzonitrile and nitrobenzene. These were the solvents used to check Eqs. (49) and (50). In the aliphatic series no such series was available; ethyl alcohol and cyclohexane were used, but for a different purpose.⁵⁶ Other solvents were tried and abandoned; thus, ethyl bromide (B.P. 38°C) was so volatile that evaporation produced serious errors; decahydronaphthalene behaved too much like cyclohexane to be of interest; ethyl acetate, otherwise eminently suitable, was doubtful geometrically; and so forth.

Suitable active substances were easier to find, the only requirements being purity and absence of tautomerism. Diacetyl diethyl tartrate was chosen, not only because of the reasons outlined in Section 7 (Part II, E), but also because its known susceptibility to solvent influences made us anticipate fairly large changes of rotation and correspondingly good precision. *d*-Camphor and *d*-limonene were selected because of their availability in quantity and purity. 1-Menthol was tried for a series of experiments, but its relative insensibility towards external influences made it impossible to draw conclusions from its behavior.

II. Experimental procedure

Fixed amounts (± 10 milligrams) of active substance were weighed into a set of 50 cc graduated flasks. Varying quantities of a polar solvent were added to the flasks, which were then weighed, and filled up to the 50 cc mark with nonpolar solvent in a thermostat at 25.00°. The resulting solutions were again weighed; the weights of the three substances in a fixed volume were then known. The flasks were calibrated and the weights corrected to vacuum.

⁵⁶ Aliphatic series measurements on diacetyl diethyl tartrate could not be made because of its small solubility (about 1 percent) in cyclohexane, *n*-heptane and decahydronaphthalene.

To minimize evaporation losses, readings were made of

$$n_{5461}^{25.00^\circ}, \epsilon_{\infty}^{25.00^\circ} \text{ and rotation }]_{5461}^{25.00^\circ}$$

as soon as possible after the solutions were made up.

P_γ was computed from the equation

$$N(\epsilon - 1/(\epsilon + 2)) = n_\alpha P_\alpha + n_\beta P_\beta + n_\gamma P_\gamma.$$

P_β was found by measurements on the pure solvent β , P_α by measurements on the two-component (α , β) mixture. Assuming that P_α and P_β were constants independent of n_γ , the values of P_γ could then be found from measurements on the 3-component mixtures.

S is very sensitive to small changes in Ω^0 , the value of the rotivity of the active material dissolved in pure solvent β , particularly in those cases where $\Omega - \Omega^0$ is not large. Ω^0 was therefore measured more than once, and the mean used. (Table V.)

TABLE IX. Diacetyl diethyl *d*-tartrate—benzene—nitrobenzene.

$G(\beta, \gamma) = -543.4$		$K_\gamma = 2.750$		$50M_\gamma = 6152.5$
w_γ	$\frac{-G(\beta, \gamma)}{50M_\gamma} w_\gamma$	$\frac{K_\gamma}{50M_\gamma} w_\gamma P_\gamma$	$\frac{w_\gamma}{50M_\gamma} \times [G(\beta, \gamma) + K_\gamma P_\gamma]$	observed
1.197	0.1057	0.1685	.0628	.054
2.469	0.2181	0.3203	.1022	.072
2.472	0.2184	0.3204	.1020	.102
3.587	0.3169	0.4406	.1237	.160
4.744	0.4191	0.5489	.1298	.130
4.824	0.4262	0.5586	.1324	.142
5.975	0.5278	0.6578	.1300	.127
5.996	0.5297	0.6583	.1286	.142
7.349	0.6492	0.7637	.1145	.109
9.573	0.8457	0.9149	.0692	.064
12.008	1.0608	1.0605	-.0003	.015
14.383	1.2706	1.1812	-.0894	-.081
16.788	1.4831	1.2915	-.1916	-.182
17.998	1.5899	1.3435	-.2464	-.221
24.004	2.1205	1.5621	-.5584	-.555
29.975	2.6480	1.7446	-.9034	-.914
54.77	4.8384	2.3126	-2.5258	-2.525

TABLE X. Diacetyl diethyl *d*-tartrate—benzene—benzonitrile.

$G(\beta, \gamma) = -84.11$		$K_\gamma = 2.098$		$50M_\beta = 5152.5$
w_γ	$\frac{-G(\beta, \gamma)}{50M_\gamma} w_\gamma$	$\frac{K_\gamma}{50M_\gamma} w_\gamma P_\gamma$	$\frac{w_\gamma}{50M_\gamma} \times [G(\beta, \gamma) + K_\gamma P_\gamma]$	observed
5.023	0.0820	0.4980	.4160	.416
6.019	0.0983	0.5677	.4694	.490
8.046	0.1313	0.6914	.5601	.560
10.047	0.1640	0.7944	.6304	.628
12.549	0.2048	0.9051	.7003	.683
15.062	0.2459	1.0008	.7549	.752
20.092	0.3280	1.1583	.8303	.810
30.107	0.4915	1.4047	.9132	.913
45.760	0.7470	1.7034	.9564	1.067

III. Preparation of materials

Diacetyl diethyl d-tartrate.—Diethyl *d*-tartrate was made from *d*-tartaric acid and absolute ethyl alcohol according to the method of Lowry and Cutter.⁵⁷ The crude product was distilled at 2 mm, retaining only the colorless middle fraction, $\alpha_{5461}^{25} = 9.87^\circ$ (2 dm). This was refluxed with acetic anhydride, following the procedure of McCrae and Patterson,⁵⁸ giving diacetyl diethyl *d*-tartrate. The crude product was purified⁵⁹ by recrystallizing 5 times from aqueous alcohol.⁶⁰ M.P. 67.3–67.6°C (corr.). $[\alpha]_{5461}^{25}$ ($c = 10.01$ in benzene) = -14.41° . Analysis: Calculated, C = 49.61

TABLE XI. *d*-Camphor—benzene—nitrobenzene.

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
5.006	39.02	00.000	10.903	1.49675	.4053	12.841	—
5.008	35.02	4.789	10.988	1.50130	.5565	12.892	224.4
5.005	30.37	11.98	11.075	1.50813	.6872	12.942	175.1
5.008	25.95	17.99	11.198	1.51374	.7529	13.028	149.4
5.004	8.483	42.038	11.420	1.53628	.8802	13.082	100.0
5.006	0.000	53.65	11.470	1.54704	.9099	13.039	88.38

d-Camphor—benzene—chlorobenzene.

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
5.006	39.02	00.000	10.903	1.49675	.4053	12.841	—
5.004	00.00	49.33	10.880	1.52019	.6359	12.609	56.65

TABLE XII. *d*-Limonene—benzene—chlorobenzene.

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
4.200	39.115	0.000	28.880	1.49627	.3004	33.534	—
4.205	34.761	5.507	23.978	1.49903	.3482	33.566	79.09
4.202	30.430	11.034	24.015	1.50177	.3901	33.576	75.90
4.201	26.031	16.558	24.073	1.50450	.4270	33.601	73.31
4.197	21.690	22.073	24.115	1.50720	.4592	33.627	70.75
4.197	17.380	27.550	24.160	1.50978	.4880	33.629	68.56
4.196	00.000	50.537	24.343	1.52055	.5876	33.625	61.65

TABLE XIII. *d*-Camphor—cyclohexane—ethanol.

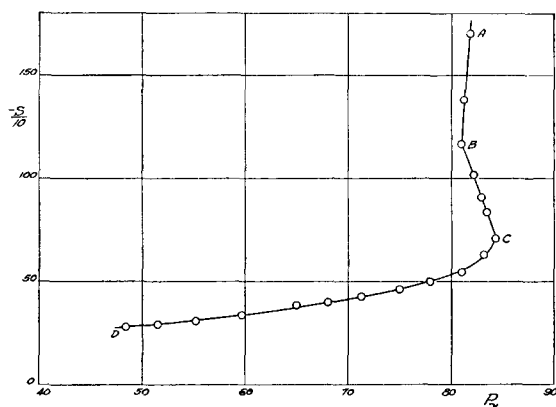
w_α	w_β	w_γ	Rotation	n	r	Ω	$-S/10$	P_γ
5.006	34.67	0.000	15.107	1.42981	.3654	18.654	—	—
5.005	33.80	0.832	14.590	1.42821	.3893	18.040	169.9	81.92
5.006	33.04	1.563	14.315	1.42672	.4099	17.715	138.3	81.32
5.008	32.24	2.374	14.095	1.42542	.4330	17.427	119.0	80.99
5.008	31.42	1.175	13.918	1.42353	.4575	17.225	101.5	82.24
5.007	30.68	3.938	13.775	1.42203	.4812	17.100	90.86	83.03
5.006	29.90	4.740	13.628	1.42074	.5060	16.936	83.45	83.50
5.009	28.26	6.304	13.433	1.41755	.5543	16.722	70.57	84.33
5.007	26.73	7.897	13.222	1.41498	.5986	16.495	62.95	83.18
5.005	24.776	9.886	13.045	1.41163	.6487	16.320	54.36	81.12
5.008	22.83	11.835	12.825	1.40809	.6888	16.075	50.17	78.01
5.004	20.889	13.813	12.642	1.40535	.7256	15.889	46.09	75.04
5.005	18.96	15.79	12.475	1.40144	.7512	15.720	42.78	71.31
5.007	16.933	17.842	12.337	1.39812	.7762	15.556	39.72	68.05
5.006	15.30	19.73	12.160	1.39572	.7952	15.382	38.18	65.00
5.005	11.185	23.717	11.977	1.39073	.8261	15.207	33.46	59.70
5.005	7.375	27.664	11.735	1.38294	.8489	14.982	30.56	55.16
5.005	3.555	31.621	11.442	1.37737	.8684	14.665	29.05	51.50
5.005	0.000	35.326	11.202	1.37241	.8798	14.408	27.67	48.36

⁵⁷ T. M. Lowry and J. O. Cutter, J. Chem. Soc. 121, 532 (1922).

⁵⁸ J. McCrae and T. S. Patterson, J. Chem. Soc. 77, 1098 (1900).

⁵⁹ O. Scheuer, Zeits. f. physik. Chemie 72, 516 (1910).

⁶⁰ Dipropionyl diethyl *d*-tartrate, a liquid, made in an analogous fashion, could not be purified.

FIG. 12. *d*-Camphor in cyclohexane-ethanol mixtures.

percent, H=6.25 percent; found, C=49.78 percent (mean of 4), H=6.94 percent (mean of 3).

d-Camphor.—Eastman block camphor was recrystallized from aqueous alcohol, carefully removing last traces of moisture by extended drying in air and finally by heating at 110° for 30 minutes. $[\alpha]^{25}_{5461}$ ($c=10.012$ in benzene) = 74.64°.

d-Limonene.—Eastman *d*-limonene was fractionally distilled at 25 mm pressure, keeping only the middle fraction, B.P. 79–80°C. $[\alpha]^{25}_{5461}$ ($c=8.356$ in benzene) = 143.2°.

Cyclohexane.—Eastman cyclohexane was dried over sulfuric acid and fractionated,⁶¹ retaining the middle fraction B.P. 80.0–80.6°, $\epsilon_{\infty}^{25}=2.021$.

Ethanol.—Commercial absolute alcohol (U.S.P.), unsuitable for dielectric measurements because of conductivity,

TABLE XIV. *d*-Camphor—cyclohexane—benzene.

w_{α}	w_{β}	w_{γ}	Rotation	n	Ω	moles benzene
5.006	34.67	0.000	15 107	1.42981	18.654	.00000
5.001	30.751	4.334	14 524*	1.43661	17.866	.05553
5.007	26.77	8.702	14.010	1.44273	17.139	.1115
5.001	22.931	13.055	13 492*	1.45025	16 437	.16727
5.007	19.01	17.42	13.095	1.45693	15 860	.2233
5.000	15.231	21.746	12 562*	1.46529	15 146	.27863
5.006	26.13	26.13	12.172	1.47233	14 585	.3348
4.998	7.571	30.446	11.731*	1.48134	13.991	.39010
4.999	3.761	34.802	11.335*	1.48957	13.437	.44591
5.006	0.000	39.02	10.903	1.49675	12.841	.4999
5.001	0.000	39.094	10 894*	1.49808	12.831	.50090

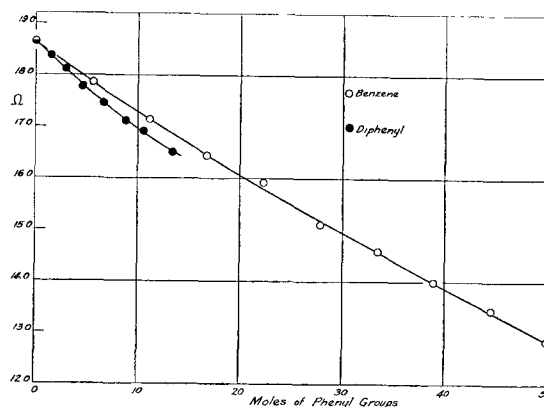
* The rotations have been corrected for racemization.

TABLE XV. *d*-Camphor—cyclohexane—diphenyl.

w_{α}	w_{β}	w_{γ}	Rotation	n	Ω	2 × moles diphenyl
5.006	34.67	0.000	15.107	1.42981	18 654	.00000
5.001	33 808	1.133	14.914*	1.43430	18 376	.01471
5.002	32 981	2.226	14.746*	1.43832	18.114	.02889
5.005	32.253	3.562	14.533	1.44296	17.783	.04624
5.001	30.794	5 118	14.319*	1.44884	17.462	.06643
5.005	29.588	6.791	14.105	1.45504	17.112	.08815
5.004	28 506	8.101	13.983*	1.45992	16.909	.10515
5.009	26.81	10.32	13.735	1.46797	16.499	.13396

* The rotations have been corrected for racemization.

⁶¹ All fractionations were performed using an all-glass distilling apparatus with a 10-inch Vigreux column.

FIG. 13. *d*-Camphor in cyclohexane-benzene and cyclohexane-diphenyl mixtures.

was refluxed for 4 hours with CaO and KOH, distilled, and fractionated, retaining only the middle fraction, B.P. 78.0–78.1°, $n^{25}_{5461}=1.36122$.

Benzene.—Thiophene-free benzene was dried with anhydrous CaSO₄ for 2 days, and fractionated, retaining the middle fraction, B.P. 79.6–80.0°.

Chlorobenzene.—Eastman chlorobenzene was dried with anhydrous CaSO₄ for 2 days, fractionated, keeping the fraction B.P. 131.0–131.4°. $\epsilon_{\infty}^{25}=5.596$ –5.606, ($\epsilon_{\infty}^{25}=2.2725$ for benzene as standard).

Nitrobenzene.—Nitrobenzene from benzene crystals was washed for 10 hours with normal K₂CO₃ solutions, then with water, dried 2 days with anhydrous CaSO₄, and distilled at 3 mm pressure in the all-glass fractionating apparatus. The middle fraction, a pale yellow-green, was retained.

Benzonitrile.—Schuchardt benzonitrile was fractionated, discarding a generous first fraction (to eliminate water). B.P. 189.2–190.4°.

Diphenyl.—Commercial diphenyl was recrystallized from benzene, M.P. sharp at 70.5°.

Diacetyl diethyl tartrate was recovered from solutions containing benzene, chlorobenzene and nitrobenzene by evaporating the solutions to dryness in a current of air at room temperature, washing in practical "heptane" until the odor of nitrobenzene had disappeared, and recrystallizing from aqueous alcohol. It had the same constants as the original sample, and was re-used. Cyclohexane was recovered

TABLE XVI. Diacetyl diethyl tartrate in various solvents ($c=5$ to 6).*

Solvent	$[\alpha]_D$
(pure liquid)	5.0
Alcohol (95%)	1.3
Alcohol (Abs.)	0.3
Acetone	0.1
Carbon tetrachloride	−7.8
Chloroform	−10.3
Benzene	−10.9

* P. Freundler, Ann. chim. phys. (7) 4, 244 (1895).

from solutions containing ethyl alcohol and camphor by washing with water, extracting the camphor completely with repeated portions of concentrated sulfuric acid, and fractionating. The product had no rotatory power and the same constants as the original sample, and was re-used.

IV. Apparatus and precision

Rotation was measured with a triple-field half-shadow Schmidt and Haensch polariscope, reading to 0.01° . Refractive index was measured with a Pulfrich refractometer. The light source common to both instruments was a mercury vapor lamp. For the polariscope the light was filtered through two Corning Glass Filters, No. 351 (3.5 mm) Didymium No. 512 (7.23 mm), and a nickel chloride solution to isolate the 5461 Hg line. The temperature of the solutions measured was kept at $25.00 \pm 0.02^\circ$ by a rapid current of water.

Dielectric constant was measured by the heterodyne beat method,⁶² using a $1000 \mu\mu f$ calibrated precision condenser reading to $0.1 \mu\mu f$. A standard cell was used to eliminate apparent variations in capacity caused by accidental changes in the frequency of the oscillations: changes in frequency were shown by the reading for the standard cell and corrections were made according to a previously determined calibration curve. The standard cell was a large air condenser made of concentric platinum cylinders, having a capacity of about $122 \mu\mu f$; the measuring cells were smaller, having capacities (with air as a dielectric) of 74 and $33 \mu\mu f$, and holding a volume of liquid of about 25–30 cc. The cells were immersed in an oil-bath kept at $25.00 \pm 0.01^\circ C$.

The refractive indices may vary by 5 in the fifth decimal place. Four readings were taken of each rotation, and the average deviation was 0.005° . $r = (\epsilon - 1)/(\epsilon + 2)$, computed from eight readings, can be measured to about 0.07 percent to 0.04 percent, the precision increasing with increasing ϵ .

⁶² C. P. Smyth, reference 47, p. 55.

SUMMARY

1. The theoretical method used by C. G. Darwin in his paper "The Optical Constants of Matter" is extended to the field of molecular optics. Explicit account is taken of the effect of intermolecular forces on these constants (Section 2).
2. On the basis of the concept of deformation, a relation is found between the rotivity and the average molecular field on a molecule (Section 3).
3. The expression for the average field is derived for the limiting case of a continuous medium (Section 4).
4. A more general derivation of the average field, based on statistical mechanics, is given for a simple molecular model. This field is found to be, for gases

$$(2\mu_\alpha/d^3) \cdot ((\epsilon - 1)/(\epsilon + 2)).$$

For liquids an analogous expression is found, in terms of the molar polarizations (Sections 5 and 6).

5. Combining our results, we find a relation between the rotivity and the dielectric constant, for gases, and between rotivity and molar polarization, for liquids (Section 6).

6. These results were verified by experiments (Section 7).

7. The validity of the use of the change of rotivity as a measure of the molecular field is established.