THE OPTICAL ACTIVITY OF LIQUIDS AND GASES.

BY FRANK GRAY.

THE natural activity of isotropic substances has been an interesting subject both to the chemist and to the physicist. Each has attacked the problem according to his own particular method; but unfortunately, the two lines of attack have not met. On the chemical side Pasteur, Le Bel and van't Hoff developed the present conception of molecular structure and proposed the theory connecting optical activity with an asymmetric structure of the molecule, a theory confirmed by the enormous amount of experimental work carried out in recent years. In the domain of physics the subject has been treated more from the optical view point and Drude and Voigt have shown just what form of electro-magnetic equations must hold in an active medium in order to produce rotation. However, the two theories have not been tied together; it has not been shown why the asymmetric molecule should give rise to these particular equations.

It was for this reason that the present study of optical activity was taken up. Part I. of the present paper is a brief report of a theoretical study of a few types of molecules, a study which has led to a very natural and satisfactory explanation of both the chemical and the physical facts of optical activity. Part II is a report of an experimental search for phenomena predicted from the theory.

PART I. THEORETICAL.

In the three-dimensional formulæ of chemistry, a symmetrical molecule is one that can be divided into two similar halves by a single plane, an asymmetrical molecule cannot so be divided. An enormous amount of work has been done on molecular structure by other methods than those of optical activity and the results have supported the theory that only an asymmetrical molecule can cause rotation.

If we accept, in general, the three-dimensional formulæ as representing molecular structure, then the experimental facts of optical activity may be stated as follows:

1. Any substance whose molecules are asymmetrical causes rotation. This is true for all carbon compounds, internal compensation and indirect asymmetry giving rise to only apparent exceptions.[1] Rotation has also

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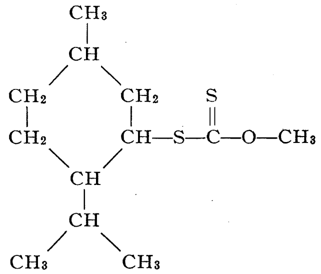
[1] "Stereo Chemistry," A. W. Stewart, 44, 83, 105.

been observed in compounds of nitrogen, sulphur, selenium, tin, and silicon.

2. Antipodes, a molecule and its mirror image, rotate in opposite directions.

3. Symmetrical molecules are not active,[1] pseudo-asymmetry and a few other cases are only apparent exceptions.

4. Absorption systems in an active substance cause anomalies in the rotary dispersion, although the origin of the band may lie in a part of the molecule distant from the central carbon atom.[2] Thus for example, in the menthyl ester of methyl dithio carbonic acid the asymmetric atom is in the ring group, while the absorption center is in the group $S = C$.



5. The magnitude of the activity is profoundly influenced by the molecular structure and is roughly dependent on the magnitude of the asymmetry of the molecule.

6. Activity varies with temperature[3] and pressure, and with the concentration of active molecules.

In attempting to account for the general facts of optical activity, new terms have been added to the field equations.[4] Thus Dude, Voigt, and Lorentz write the first equation for an active medium

$$\text{curl } H = \frac{1}{C}(\epsilon \dot{E} - f \text{ curl } \dot{E}), \tag{1}$$

according to Lorentz the second field equation remains unchanged,[5]

$$\text{curl } E = -\frac{1}{C}\dot{H}. \tag{2}$$

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[1] "Stereo Chemistry," A. W. Stewart, 21.

[2] Cotton, Ann. Chim. et d. Phys., 8, 374, 1896. Tuchugaff and Ogordnikoff, Zeit. für Phys. Chem., 74, 503, 1910, and 85, 481, 1913.

[3] Landolt, "Optical Rotation of Organic Substances," 206.

[4] Landolt, "Optical Rotation of Organic Substances," 169.

[5] Lorentz, Versuch einer Theor. der elekt. und optik. Erscheinungen.

Drude and Voigt have decided from energy considerations that the second equation should be

$$\text{(3)} \qquad \operatorname{curl} E = -\frac{1}{C}\left(\dot{H} + \frac{f}{C}\ddot{E}\right).$$

The solution of 1 with either 2 or 3 for a plane polarized wave shows that the electric vector E is rotated as the wave passes through the medium, the amount of the rotation being half as great when the Lorentz equations are used.

For the case of a plane polarized light wave these equations may be interpreted as stating that a space rate of change of E in the direction of propagation produces a component of electric polarization normal to both E and the direction of propagation, a component that does not exist in a non-active medium. In the following work we shall denote this component by P_n.

Drude has shown that the modified field equations would result if the paths of some of the electrons in an active medium were short helices all twisted in the same direction and with axes oriented at random in space, but he made no attempt to show how the asymmetrical structure of the molecule causes these spiral tracks, and thus his theory does not tie up with molecular structure, nor does it account for the anomalous rotary dispersion of the metallic tartrates and such cases as the one mentioned above. It was for this reason that the following study of the interaction between atoms was made in the hope that such interactions might afford a more satisfactory explanation of optical activity.

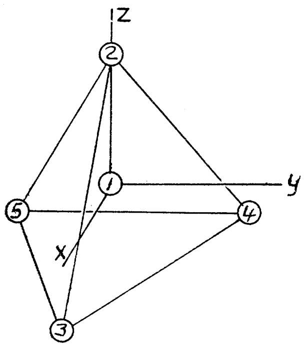

Fig. 1.

A Molecule of Five Atoms.

Consider a molecule consisting of a central atom with four other atoms grouped about it. The origin of a coördinate system (Fig. 1) will be taken at the central atom, and the axes so oriented that atom 2 will lie on the z axis and atom 3 in the xz-plane. The position of the nth atom is determined by x_n, y_n, z_n, and its distance from the origin by r_n. The distance from the nth to the mth atom is d_{nm}.

It is assumed that the atoms may be electrically polarized in any direction by an electric force and that

$$\text{(4)} \qquad p_{xn} = K_n E_x, \text{ etc.,}$$

where p_{xn} is the x component of polarization of the nth atom and K_n is a quantity depending on the atom, the molecule in which the atom occurs, and on the frequency of the wave. K_n is to be thought of as the restoring coefficient that would exist if the nth atom could be made to oscillate electrically while all the other atoms remained unpolarized. It, therefore, does not contain any terms depending on the interactions of the electrical oscillations of the atoms, but it might contain terms depending on the static forces that hold the atoms together. For mathematical simplicity it is also assumed that the atoms are small compared to the distances between them; the atoms may thus be treated as electric doublets.

When a train of light waves passes over such a molecule it will tend to polarize the atoms in the E direction. The polarized atoms will then interact in a complicated manner, and as a result the molecule as a whole will not be polarized directly in the direction of the original E of the wave and the plane of vibration of the wave will be twisted a little out of its original direction. A molecule with some other orientation may twist the plane of vibration in the opposite direction. The problem is to determine if there will be any resultant rotation when plane polarized light passes through an aggregate of such molecules oriented at random in space.

The method of attacking the problem will be to find the component of polarization of a single molecule in the N direction, *i. e.*, normal to E and the direction of propagation, and then find the average of this component for all orientations of the molecule. The polarization P_n of the medium will be found by multiplying this average value by the number of active molecules per unit volume. The polarization of the medium in the E direction will be found in the usual manner. Thus the polarization of the medium will be completely known and it should be possible to write out the field equations which will hold in the medium for a plane polarized light wave. It is evident that if P_n is different from zero the medium will be active.

The vector expressions[3] for the forces at a distance r from an oscillating doublet are

$$(5)\qquad \begin{aligned} E &= \frac{1}{r^3}\{3p_r r_1 - p\} + \frac{1}{r^2}\{3\dot{p}_r - \dot{p}\} - \{\ddot{p} r_1 - p\} \\ H &= -\frac{1}{r^2}[r_1\dot{p}] - \frac{1}{r}[r_1\ddot{p}], \end{aligned}$$

where p_r is the polarization in the r direction and r_1 is a unit vector in the

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[1] Drude, Gött. Nachr., 1904, I., 1.

[2] Drude, "Lehrbuch der Optik," 338.

[3] Abraham, "Theorie der Elektrizatät," II., 63.

r direction. Since r is small compared to the wave-length of light, all terms but the $1/r^3$ terms will be neglected. This term is only the ordinary electro-static force of a doublet. Let p_{xm}, p_{ym}, p_{zm} be the components of polarization of the mth atom whose coördinates are x_m, y_m, z_m, and let d_{nm} be the distance to the nth atom whose coördinates are x_n, y_n, z_n. Then, the components of force at atom n due to the polarization of atom m are

$$\begin{aligned} E_x &= \frac{1}{d_{nm}^3}\left\{\frac{3}{d_{nm}^2}(x_n - x_m)[p_{xm}(x_n - x_m) + p_{ym}(y_n - y_m) \right. \\ &\qquad\qquad \left. p_{zm}(z_m - z_n)] - p_{xm}\right\}, \\ E_y &= \frac{1}{d_{nm}^3}\left\{\frac{3}{d_{nm}^2}(y_n - y_m)[\cdots] - p_{ym}\right\}, \\ E_z &= \frac{1}{d_{nm}^3}\left\{\frac{3}{d_{nm}^2}(z_n - z_m)[\cdots] - p_{zm}\right\}. \end{aligned} \tag{6}$$

Let x', y', z' be a fixed coördinate system to which the plane polarized light wave is referred. The z' axis will be taken in the direction of propagation, the x' axis in the E direction, and the y' axis in the N direction. The x, y, z system in which the molecule is fixed, will be referred to the x', y', z' system by the angles ϕ, β, θ of Fig. 2.

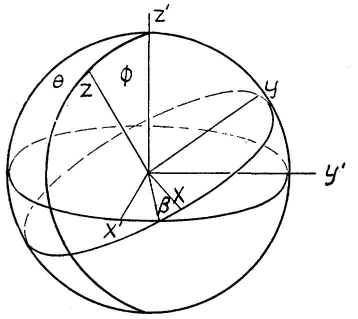

Fig. 2.

Let the electric force of the wave be given at the origin by

$$E_{x'} = E_{x'} \cos \nu t, \text{ etc.}$$

Then the external force on the nth atom is

$$E_{x'} = E_{x'} \cos\left(\nu t - \frac{\nu}{c} z_n'\right), \text{ etc.} \tag{7}$$

The total force acting on an atom has the same period as the wave; so the polarization of the mth atom may be written

$$\begin{aligned} p_{xm} &= P_{xm} \cos (\nu t - \delta_{xm}), \\ p_{ym} &= P_{ym} \cos (\nu t - \delta_{ym}), \\ p_{zm} &= P_{zm} \cos (\nu t - \delta_{zm}). \end{aligned} \tag{8}$$

The electro-static action of one atom upon another will be retarded, thus the force exerted upon atom n by atom m at the time t will be due to the retarded state

$$p_{xm} = P_{xm} \cos\left(\nu t - \delta_{xm} - \frac{\nu}{c} d_{nm}\right), \text{ etc.} \tag{9}$$

In the equation for the polarization of an atom,

$$\frac{1}{K_n} p_{xn} = E_x, \text{ etc.,} \tag{4}$$

the electric force includes that of the wave and also the forces arising from each component of polarization of the other four atoms. Using equations 6, 7 and 9 to determine the total force acting on an atom n, equation 4 becomes

$$\begin{aligned} \frac{1}{K_n} \cos(\nu t - \delta_{xn}) &= E_x \cos\left(\nu t - \frac{\nu}{c} z_n'\right) \\ &+ \sum_{m=1}^{5} \frac{1}{d_{nm}^3} \left[\frac{3(x_n - x_m)^2}{d_{nm}^2} - 1 \right] \cos\left(\nu t - \delta_{xm} - \frac{\nu}{c} d_{nm}\right) P_{xm} \\ &+ \frac{3}{d_{nm}^2} (x_n - x_m)(y_n - y_m) \cos\left(\nu t - \delta_{ym} - \frac{\nu}{c} d_{nm}\right) P_{ym} \\ &+ \frac{3}{d_{nm}^2} (x_n - x_m)(z_n - z_m) \cos\left(\nu t - \delta_{zm} - \frac{\nu}{c} d_{nm}\right) P_{zm}, \end{aligned} \tag{10}$$

where the summation excludes the nth atom. After expanding the cosine terms, the equation reduces to

$$(\cdots) \cos \nu t + (\cdots) \sin \nu t = 0.$$

The quantities inside the bracket are independent of t; therefore each must be equal to zero. If we let

$$P_{xm} \cos \delta_{xm} = A_{xm},$$
$$P_{xm} \sin \delta_{xm} = B_{xm},$$

these conditions are expressed by the equation

$$\begin{aligned} \frac{1}{K_n} A_{xn} = E_x \cos \frac{\nu}{c} z'_n &+ \sum_{m=1}^{5} \frac{1}{d_{nm}^3} \cos \frac{\nu}{c} d_{nm} \left\{ \left[\frac{3(x_n - x_m)^2}{d_{nm}^2} - 1 \right] A_{xm} \right. \\ &\left. + \frac{3}{d_{nm}^2} (x_n - x_m)(z_n - z_m) A_{ym} + \frac{3}{d_{nm}^2} (x_n - x_m)(z_n - z_m) A_{zm} \right\} \\ &- \frac{1}{d_{nm}^3} \sin \frac{\nu}{c} d_{nm} \left\{ \left[\frac{(3x_n - x_m)^2}{d_{nm}^2} - 1 \right] B_{xm} + \frac{3}{d_{nm}^2} (x_n - x_m)(y_n - y_m) B_{ym} \right. \\ &\left. + \frac{3}{d_{nm}^2} (x_n - x_m)(z_n - z_m) B_{zm} \right\}, \end{aligned}$$

and a similar one for $1/K_n(B_{xn})$ in sine terms but with the A's and B's interchanged. There are thus thirty linear equations to solve for the thirty A's and B's.

In forming the determinant the unknowns may be numbered as follows:

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & \cdots & 15 \\ A_{x1} & A_{y1} & A_{z1} & A_{x2} & & A_{z5}, \\ 16 & 17 & 18 & 19 & \cdots & 30 \\ B_{x1} & B_{y1} & B_{z1} & B_{x2} & & B_{z5}, \end{array}$$

and the equations may be numbered

$$\frac{1}{K_1}A_{x1} = E_x \cos\frac{v}{c}z_1' + \Sigma \tag{1}$$

$$\frac{1}{K_1}A_{y1} = \underline{\hspace{3cm}} \tag{2}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\frac{1}{K_5}A_{z5} = \underline{\hspace{3cm}} \tag{15}$$

$$\frac{1}{K_1}B_{x1} = \underline{\hspace{3cm}} \tag{16}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\frac{1}{K_5}B_{z5} = \underline{\hspace{3cm}}. \tag{30}$$

The following relations hold among the minors of the general determinant. If D_r^h is the minor formed by suppressing the rth row and the nth column, then

$$\begin{aligned} D_r^h &= D_h^r, \\ D_r^h &= D_{h+15}^{r+15}, \\ D_r^h &= -\,D_{r+15}^{h-15}, \\ D_{r+15}^h &= -\,D_{r+\ 5}^h, \\ D_{r-15}^{h+15} &= D_r^h. \end{aligned}$$

The value of any unknown, number m, may be found by substituting the constants for the mth column and dividing by D. The following is the solution for A_{x1} after expanding the numerator by minors with respect to the column of constants.

$$\begin{aligned} A_{x1} = \frac{1}{D}\Bigg\{ & E_xD_1^1 - E_yD_1^2 + E_zD_1^3 - E_xD_1^4\cos\frac{v}{c}z_2' \\ & + E_yD_1^5\cos\frac{v}{c}z_2' + \cdots E_xD_1^{16} + E_yD_1^{17} - E_zD_1^{18} \\ & + E_xD_1^{19}\sin\frac{v}{c}z_2' - E_yD_1^{20}\sin\frac{v}{c}z_2' + \cdots \Bigg\}. \end{aligned}$$

There will be similar solutions for all the other A's and B's.

If the solution A_{xm} be multiplied by cos νt and that of B_{xm} by sin νt and combined using the relation between minors given above and also letting

$$R_r^h = \sqrt{(D_r^h)^2 + (D_r^{h+15})^2},$$

then

$$P_{xm} = \frac{1}{D}\Big\{ \sqrt{2}[\pm E_x R_m' \cos(\nu t - \epsilon) \pm E_y R_m^2 \cos(\nu t - \epsilon) \pm E_z R_m^2 \cos(\nu t - \epsilon)] \pm E_x R_m^4 \cos\left(\nu t - \frac{\nu}{c} z_2' - \epsilon\right) \pm \cdots \Big\}, \tag{11}$$

where all the ϵs are different. An example of one ϵ is

$$\epsilon = \tan^{-1}\frac{D_1^5}{D_1^{20}}.$$

It is found that the ϵs do not occur in the final result, and they are thus of little interest.

The undetermined signs of equation 11 could be determined in an actual case by going back to the physical meaning of equation 3. Even in the present general case the sign of a great many of the terms may be found. There are fifteen such equations, one for each component of polarization of the five atoms.

The total polarization of the molecule in the N direction, *i. e.*, $P_{y'}$ may be found by projecting the components of polarization of each atom on the y' axis and taking the sum for all atoms in the molecule. The average of this polarization $\overline{P_{y'}}$ for molecules oriented at random, may be shown to be

$$\overline{P_{y'}} = \frac{1}{8\pi^2}\int_0^{2\pi} d\phi \int_0^{2\pi} d\beta \int_0^{\pi} P_{y'} \sin\theta d\theta,$$

where, of course, $P_{y'}$ will be a function of ϕ, β, θ. Before integrating it is necessary to express E_x, E_y, E_z occurring in $P_{y'}$ in terms of $E_{y'}$ and also to express z_n' in terms of x_n, y_n, z_n.

In order to carry out the integration the following approximation is made

$$E_{x'} \cos\left(\nu t - \frac{\nu}{c} z_m' - \epsilon\right) = E_{x'} \cos(\nu t - \epsilon) - \frac{\partial E_{x'}}{\partial z'} z_n', \text{ etc.}$$

It may be shown that ϵ expresses the lag of the retarded interaction behind the E of the wave and that it is very small compared to 2π. So $\partial E_{x1}/\partial z'$ will be practically constant for such a short time and the approximation is justified.

There will be 225 terms in $\overline{P_{y1}}$ similar to

$$\frac{1}{8\pi^2}\int_0^{\pi} d\varphi \int_0^{\pi} d\theta \int_0^{2\pi} \frac{R_m{}^4}{D} (\cos\phi\cos\theta\cos\beta - \sin\beta\sin\theta)(\cos\beta\cos\phi\sin\theta$$
$$+ \sin\phi\cos\theta)\left\{ E_{x'}\cos(\nu t - \epsilon) - \frac{\delta E_{x'}}{\partial z'}(-x_2\cos\beta\sin\varphi\right.$$
$$\left. + y_2\sin\beta\sin\varphi + z_2\cos\varphi \right\} \sin\varphi\, d\beta.$$

In the integration all terms will vanish except certain ones containing $\partial E_{x1}/\partial z'$. The final result is

$$\overline{P_y'} = \frac{1}{12D}\frac{\partial E_{x'}}{\partial z'}[z_2\{(\pm R_1{}^5 \pm R_2{}^4) \pm (R_7{}^5 \pm R_8{}^4) \pm (R_{10}{}^5 + R_{11}{}^4)$$
$$\pm (R_{13}{}^5 + R_{14}{}^4) + x_3\{\cdots\} + z_3\{\cdots\} + \cdots + z_5\{\pm (R_1{}^{14} + R_2{}^{13}) \tag{12}$$
$$\pm (R_4{}^{14} + R_5{}^{13}) \pm (R_7{}^{14} + R_8{}^{13}) \pm (R_{10}{}^{14} + R_{11}{}^{13})\}].$$

It may be shown that this expression is not identically equal to zero. Thus $\overline{p_{y'}}$ will, in general, be different from zero and the medium will have a component of polarization in the N direction. As stated previously, this means that the medium will be active.

In equation 12 let

$$b = \frac{1}{12D}[\cdots],$$

then

$$\overline{P_{y'}} = b\frac{\partial E_{x'}}{\partial z'}.$$

If n is the number of active molecules per unit volume, then the polarization in the N direction will be

$$P_H = nb\frac{\partial E_{x'}}{\partial z'}.$$

This is for the special case of axes x', y', z' taken in the direction of propagation of the wave and in the H and E directions respectively. For any set of axes this equation may be shown to be

$$P_H = nb \operatorname{curl} E.$$

The polarization in the E direction is

$$P_E = E\Sigma\frac{e^2/m}{\nu_0{}^2 - \nu^2} = E\Sigma,$$

Where ν_0 is the natural frequency of an electron in the medium, e is the electronic charge, and m is the electronic mass. The summation is taken over all electrons in unit volume. It is to be noted that this summation is the same one that occurs in the theory of refractive indices and that it is taken over both active and non-active molecules in the medium. The interaction between atoms in the same molecules has been taken care of in ν_0, for ν_0 means the frequency of an electron as it occurs in the molecule and not the frequency it would have in the isolated atom.

The total polarization is

$$P = P_N + P_E = E\Sigma + nb \operatorname{curl} E.$$

In this equation we have neglected the fact that the force acting on an electron in a material medium is really not E but $E + aP$, where a is usually considered to be about $4\pi/3$. Putting in this additional term

$$P = (E + aP) + nb \operatorname{curl} (E + aP).$$

Then,

$$P = E\frac{\Sigma}{1 - a\Sigma} + \frac{nb}{1 - a\Sigma}\operatorname{curl} (E + aP).$$

Put

$$P = E\frac{\Sigma}{1 - a\Sigma}$$

in the curl term; then

$$P = E\frac{\Sigma}{1 - a\Sigma} + \frac{nb}{(1 - a\Sigma)^2}\operatorname{curl} E.$$

The first field equation then becomes

$$\operatorname{curl} H = \frac{1}{c}\left(1 + 4\pi\frac{\Sigma}{1 - a\Sigma}\right)\dot{E} + \frac{4\pi}{c}\frac{nb}{(1 - a\Sigma)^2}\operatorname{curl} \dot{E},$$

and according to equation 3, the second equation should be

$$\operatorname{curl} = -\frac{1}{c}\dot{H} - \frac{8\pi}{c^2}\frac{nb}{(1 - a\Sigma)^2}\ddot{E}.$$

The solution of the two equations gives for the rotation per unit length

$$\delta = -\frac{4\pi nb}{(1 - a\Sigma)^2}\frac{\nu^2}{c^2}. \tag{13}$$

According to Lorentz, equation 2, the second field equation remains unchanged and the rotation should be half as great.

Antipodes.

It may be shown that antipodes rotate in opposite directions. The antipode of the present general molecule of five atoms may be easily treated by interchanging the positions of atoms 4 and 5 with respect to the xz-plane but letting each atom keep the same absolute valueof coördinates. If the present system of coördinates is changed into a left-handed system by reversing the y and y' axes and measuring θ and β in a left-handed sense, then all equations will hold identically in the left-handed system; so $\overline{p_y'}$ will be given by equation 12. But, with respect to the light wave, y' is now in the opposite direction to what it was for the first molecule, and the rotation will be opposite in sign but of the same magnitude as before.

The Symmetrical Molecule.

The symmetrical molecule may be most easily considered by letting atoms 4 and 5 be identical; then

$$x_4 = x_5$$

$$| y_4 | = | y_5 |$$

$$z_4 = z_5$$

$$K_4 = K_5.$$

From a consideration of the general determinant it may be shown that a great many of the Rs in Eq. 12 vanish and the remainder cancel out leaving $\overline{p_y'} = 0$. So a symmetrical molecule cannot cause rotation.

Other Molecules.

The case of a molecule containing less than five atoms is obtained by setting $K = 0$ for one or more atoms. It is found that:

A molecule of only two atoms cannot be active.

A molecule of three atoms cannot be active.

An asymmetrical molecule of four atoms would be active.

However, a molecule of this type is not known. Every known molecule of four atoms consists of a central trivalent atom with three other atoms attached to it; thus all four atoms probably lie in the same plane or at least oscillate back and forth through the same plane. In either case the molecule would be inactive. This is supported by the failure to resolve such compounds into isomeric forms.

A treatment similar to the present could be extended to molecules of more than five atoms; and from analogy with the present case it seems probable that an asymmetric molecule will be active and a symmetrical molecule inactive.

Rotatory Dispersion.

The K for an atom is the polarization of the atom by unit electric field and it may be shown that

$$K_n = \Sigma \frac{e^2/m}{\nu_0^2 - \nu^2},$$

where the summation is taken over all electrons in the nth atom. Thus K will vary with the frequency of the wave and cause rotatory dispersion. At an absorption band whose origin is in an active molecule, one of the Ks will pass through anomalous values and change sign. The factor b in equation 13 is an algebraic function of the Ks; thus we might, in general, expect the rotation to be anomalous at a band, but not necessarily in the simple manner demanded by the Drude theory. This is in agreement with the rotatory dispersion of the metallic tartrates and malates. It is conceivable that the general rotatory dispersion of a substance might prevent an absorption band from producing an anomaly just as in the case of ordinary dispersion a band does not always produce anomalous dispersion.

Bruhat[1] has shown that the term $(1 - \Sigma)^2$ in Eq. 13 cannot cause an appreciable anomaly in ordinary cases. The absorption coefficient must be of the order of that for metallic absorption before this term becomes important.

Rotation and Atomic Refractivity.

The Ks are closely connected with atomic refractivities. The molecular refractivity of a substance is defined as

$$M = \frac{m}{d}\frac{n^2 - 1}{n^2 + 1} = \text{constant.}\ \Sigma\frac{e^2/m}{\nu_0^2 - \nu^2},$$

where m is the molecular weight; d, the density; and n is the refractive index. The atomic refractivity is the contribution of each atom to this sum. In many organic compounds the atomic refractivities are approximately additive and, in such cases, the Ks are proportional to the atomic refractivities. In complex molecules it often happens that the atomic refractivities are not additive, but the summations over closely built groups are additive, and in such cases we may think of K for the whole group as being proportional to its group refractivity. There should thus be a close connection between atomic or group refractivity and optical activity; a radical with a large group refractivity should exert a greater influence upon the activity of a molecule than a radical with a smaller group refractivity.

This is well shown by the influence of the double ethylene bonding $C = C$ upon the activity of a molecule. It is well known that an ethylene group introduced into a molecule produces an abnormally high molecular refractivity, and Walder and Zilnsky[13] have shown that such a group also tends to increase the molecular activity when introduced into a molecule.

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[1] "Stereo Chemistry," Stewart, 98.

[2] Bruhat, Phil. Mag., 28, 302, 1914.

These considerations bring out clearly the reason for the failure of the Guye hypothesis[1] in so many cases. Roughly, this hypothesis states that the optical activity of a molecule is measured by its mass asymmetry. From the present theory it is evident that it is not the mass asymmetry that is important but the asymmetry in terms of atomic or group refractions that is important.

Change of Rotation with Temperature.

The activity of most substances varies rapidly with the temperature;[4] for some substances it increases; for others, it decreases and may even change sign. No attempt has been made to explain these bewildering changes, because of the lack of any adequate theory of rotation itself. There can be little doubt that, on account of thermal agitations, the atoms are vibrating about points of equilibrium inside of the molecule. However, on the Guye hypothesis, it was difficult to see how such oscillations could affect the rotation, for on the average the atom would act as if it were fixed at the position of equilibrium.

This is not true from the present point of view. The electrostatic action of two atoms varies as $1/d^3$. For such a law of force the average interaction will change with the amplitude of the oscillations and thus cause the rotation to vary with the temperature.

Without doubt other factors such as loose chemical changes also enter into the temperature effect.

PART II. EXPERIMENTAL.

On the Drude theory, only those electrons which vibrate along spiral paths give rise to anomalous rotation; on the present theory, any absorption band belonging to an electron in an active molecule might be accompanied by an anomaly. The work of Tuchugoff and Ogordnikoff referred to in the first part of this paper may be looked upon as supporting this view. It is well known that certain atomic groups called chromophores act as absorbing centers and that a colored compound is produced when one is introduced into the molecule of an otherwise colorless substance. These two experimenters have united non active radicals containing the chromophore $C = S$ with complex active radicals, and they find that the absorption bands of the resulting compounds show anomalous rotation. Although the absorption in such cases is always connected with the chromophores, the appearance and position of the band is characteristic of the molecule. So it was decided that a more severe test of the theory was desirable, and this test was carried out in the following manner.

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[1] [1]Landolt, "Optical Rotation of Organic Substances," 299.

The group of neodymium absorption bands near 5,800 and 5,200 are characteristic of the neodymium atom and are not greatly influenced by the molecule in which the atom is present. The electrons causing these bands do not vibrate along spiral paths, for such compounds as neodymium nitrate are inactive. If this atom is united with an active acid radical, will these electrons cause anomalous rotation? According to the present theory they might; while, according to the Drude theory it is difficult to see how they could cause anomalies, because they are little influenced by molecular structure.

Most organic salts of the rare earths are insoluble, but a soluble active compound of neodymium was finally obtained in the following manner. Neodymium nitrate was dissolved in a neutral solution of sodium tartrate and a crystalline substance separated out slowly. At the end of a week this was filtered off and was found to be soluble in a basic solution. Using sodium hydride the solution was made just basic enough to dissolve all the crystals. The solution was very dilute. The compound is probably a double tartrate of neodymium and sodium. It may be mentioned that the original nitrate was not very pure as it contained some lanthanum; however its presence was not objectionable in the present work.

The solution is strongly absorbing and it was difficult to measure the rotation inside of the absorption bands. As the general rotation for 8 cm. of the solution was only one degree and the absorption bands are relatively broad compared to those of a gas, it was impossible to use the quartz wedge method. It was finally decided to use a monochromatic illuminator with a divided field.

The usual form of monochromatic illuminator is not suitable for the purpose, because the maximum brightness that can be obtained for the divided field does not depend on the ratio of focal length to aperture of the collimating lens but only upon the dispersion and aperture of the prisms.[1] After several failures with different forms of apparatus, a powerful and rather simple instrument was constructed. The optical system is shown in Fig. 3. Two high dispersion prisms were used with auto-collimation to double the dispersion. The visible spectrum was spread out over almost thirty degrees of arc. The prisms were set at minimum deviation for the band to be examined and the spectrum was moved across the slit S_2 by rotating the mirror M. The collimating lens L_1 had a focal length of 52 cm. The lens L_2, of 28 cm. focal length, formed an image of a point behind the collimating lens on the divided field F and thus gave it uniform illumination. The image of the slit

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[1] Elias, Zeit. fur Instrumentenkunde, 31, 137, May, 1911.

S_2 fell upon the pupil of the eye placed at the diaphragm D. The divided field was viewed directly without the aid of an eye piece, thus saving a loss of light by reflection. Maximum brightness was secured by making the apparent size of the illuminated area of F only just large enough for settings to be made and by always keeping the slits S_1 and S_2 of the same width. A cell 8 cm. long and containing the active solution was placed at C.

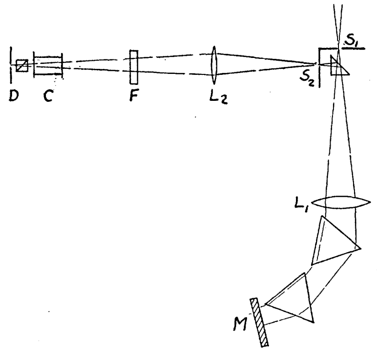

Fig. 3.

Scattered light was carefully screened out. It is impossible to get rid of all the light reflected from the collimating lens, but with the present arrangement all such light goes to form a small image of the slit, which appears as a speck in the divided field and thus causes no error.

An intensely bright field could be obtained, monochromatic to 2A°; but the absorption of the neodymium solution was so great that it was necessary to use 10 A° even with the brightest sun light. The 10 A° means the range of wave-lengths that could pass through the slit S_2 when the width of S_1 and S_2 were equal.

To prove that an apparent anomaly could not result from stray light or too great a slit width, the following test was made. A cell full of the neodymium solution was placed as an absorption cell just behind the slit of the monochromatic illuminator. An active sugar solution examined under these conditions showed no false anomaly, thus proving that there was no serious error from the two causes just named.

In the case of the original neodymium nitrate the absorption band in the yellow could be resolved into five lines: 5,716, a pair of strong lines 5,744 and 5,750, 5,784 and a weak line 5,807. There were two strong lines at 5,219 and 5,202. In the double tartrate the band in the yellow was shifted about 30 A° toward the red, and it could again be resolved into five lines: 5,733 weak, 5,770, 5,800 very strong, 5,819, 5,837. The band in the blue was shifted to 5,364 and could no longer be resolved into two components. Such changes as these are to be expected for the same reason that a change of solvent will shift and change the character of the bands. However, the bands are so characteristic of the atom that it is to be supposed that no great change takes place in the mode of vibration of the electrons.

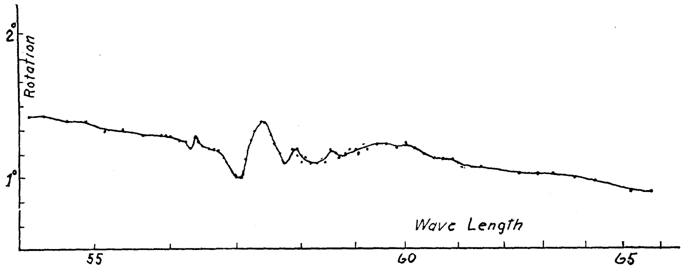

Fig. 4.

The curve shows the rotation of 8 cm. of the solution near the band 5,800.—With this depth of solution the five lines appear merged together. —The rotation is anomalous as predicted from the present theory. The large anomaly is apparently connected with the line 5,770 which is relatively weak. There are indications of anomalies in the strong absorption region covered by the three lines on the long wave-length side of the band. It is possible that larger anomalies really exist and that they have been smoothed over on account of the slit width of the illuminator. However, if all the lines tend to have anomalies of the same type, we should expect the effect to cancel out for such closely spaced lines. A small anomaly was found at 5,642, and subsequent examination showed a very faint absorption band at that wave-length. The strong band near 5,200 also showed an anomaly of the same type as the one at 5,800, but the absorption is too great for a satisfactory curve to be made.

As mentioned before, these results are in agreement with the present theory, but could hardly be explained on the Drude theory of spiral paths.

In conclusion the writer wishes to thank Professor Lehner, of the chemistry department, for his assistance in preparing an active compound of neodymium.

Summary.

Assuming that the atoms of a molecule may be electrically polarized by a light wave and that they then interact according to the ordinary laws for an electric doublet, it has been shown that the optical activity of isotropic substances may be explained as a result of such interactions.

From this view point, an asymmetric molecule will be active and a symmetrical molecule inactive. A molecule must have more than three atoms to be active.

A connection has been shown between molecular activity and atomic refractivity.

A possible explanation of the variation of rotation with temperature has been given.

According to the present view of activity any absorption band belonging to an active molecule might cause anomalous rotation.

This last statement has been tested experimentally in the most extreme case that could be obtained. A neodymium atom was introduced into an active molecule and the rotation was found to be anomalous at the bands characteristic of the atom, a result which supports the present theory.

Note.—After the theoretical part of the present paper had been completed and while the experimental work was being carried out, two excellent articles were published on the same subject by J. Stark and M. Born. Stark[1] suggested that natural activity might be explained as the result of the interaction of doublets; and later Born[1] published a mathematical treatment of the same subject. The present paper is simpler and therefore less rigorous. It may also, in a way, be looked upon as a special case of Born's more general theory; instead of an indefinite coupling the atoms have been coupled in a very definite manner. There are two important differences: (1) Born views a molecule as a system of coupled electrons, the coupling and the restoring forces being identical. In the present paper the atom is looked upon as a particle of dielectric. The atoms are coupled according to the ordinary laws for a doublet, and the restoring force on an electron is not identical with the coupling but may be influenced by it. This is supported by the fact that many absorption bands are roughly characteristic of the atom and that for many organic compounds the refractive index is an almost additive property. (2) Born neglected the retardation of the interaction between particles. This retardation might be important because the rotation depends only on a space derivative of E, *i. e.*, upon the variation of E from one side of a molecule to the other. However, the conclusions agree with those of Born, and the experimental result is a support to both theories.

In the Annalen der Physik, 48, 1, 1, September, 1915, C. W. Oseen has also presented a theoretical treatment of optical activity, very similar to that of Born.

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[1] Stark, Jahrbuch der Rad. und Elektronik., 1914.

[2] M. Born, Phys. Zeit., 16, 251, July, 1915.