[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

ON THE PRINCIPLE OF OPTICAL SUPERPOSITION.

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(PRELIMINARY COMMUNICATION.)[1]

IN THE celebrated memoir founding the science of stereochemistry,[2] van't Hoff makes an important assumption concerning the optical activities of several asymmetric carbon atoms in a molecule. Referring to molecules made up of two similar asymmetric groups,

$$\begin{array}{c} C(R_1R_2R_3) \\ | \\ C(R_1R_2R_3), \end{array}$$

he says: "The activity that each of these asymmetric carbon atoms contributes to the whole will be equal or opposite, say a and $-a$; so that the activity of the four isomers will be represented by the expressions: (1) $+a+a$, (2) $+a-a$, (3) $-a+a$, (4) $-a-a$." The assumption symbolized by these expressions is, that the two partial rotations are not themselves changed by addition to, or subtraction from, one another. Writing twenty years later,[3] van't Hoff extends this assumption to molecules with several different asymmetric carbon atoms. "Thus," he says, "for the four pentose types, $COH(CHOH)_3CH_2OH$, we should have the following rotations:

No. 1.	No. 2.	No. 3.	No. 4.
+A	+A	+A	—A
+B	+B	—B	+B
+C	—C	+C	+C."

Here again each partial rotation, A, B, C, is assumed to remain the same, whether the other partial rotations are positive or negative. In other words, *the rotation due to a given asymmetric carbon atom is assumed to be independent of the configuration of the groups around the other asymmetric carbon atoms in the molecule.*

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[1] Presented before the New York Section of the American Chemical Society on January 5, 1906.

[2] Bull. soc. chim. [2] 23, 298 (1875).

[3] Van't Hoff: "Die Lagerung der Atome im Raume," 2d ed., p. 120 (1894); English trans. by Eiloart, p. 160 (London and New York, 1898).

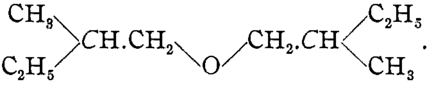
Van't Hoff's assumption was arbitrary. *A priori* it seems possible that a given dextro-rotation, A, might itself be diminished through association with a second dextro-rotation and increased through association with a levo-rotation, or *vice versa*.

In view of the fundamental importance of the assumption, Guye and Gautier[1] decided, in 1893, to subject it to careful experimental inquiry, and during the succeeding three years[2] apparently demonstrated that calculation based on that assumption yields practically the same results as direct observation. Independently of these investigators, and almost simultaneously with them, Walden[3] attacked the same problem, and by an extensive and painstaking series of observations seemed to produce even more brilliant testimony than theirs, in favor of van't Hoff's idea. The assumption, raised to the rank of "The Principle of Optical Superposition," as Guye and Gautier had designated it, was thus incorporated in stereochemistry, and to-day accounts of it may be found in all text-books.

Careful study has now led me to the conviction that a serious error of principle was involved in the experimental work of Guye and Gautier, as well as of Walden, in consequence of which their results have really no bearing on the principle of superposition. On the other hand, the few known facts that do belong within the scope of the principle, not only fail to corroborate it but rather seem distinctly to contradict it.

§1. CRITIQUE OF THE ACCEPTED EXPERIMENTAL MATERIAL.

One of the first cases studied by Guye and Gautier was that of the oxide of two active *l*-amyl radicles (di-*l*-amyl ether):



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH.CH_2\diagdown\underset{}{O}\diagup CH_2.CH<\!\!\begin{matrix}C_2H_5\\CH_3\end{matrix}.$$

The two halves of this molecule being similar (as in ordinary tartaric acid), the total optical rotation should, according to the principle of superposition, be, say, $-a-a=-2a$, and each partial rotation should be independent of the other. If, therefore, one of the partial rotations were annulled, the remaining

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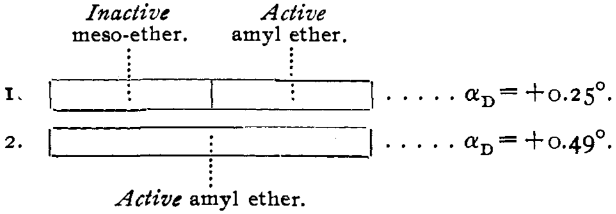
[1] Bull. soc. chim. [3] 9, 403 (1893).

[2] Compt. rend. 119, 740 and 953 (1894); Bull. soc. chim. [3] 11, 1170 (1894); Ibid. 13, 457 (1895). See also Guye and Jordan: Compt. rend. 120, 632 (1895); Guye: Ibid. 121, 827 (1895); Ibid. 122, 932 (1896).

[3] Z. physik. Chem. 15, 638 (1894); Ibid. 17, 720 (1895).

rotation should be exactly one-half the original total rotation. Now, a rotation, —*a*, of *l*-amyl can be counterbalanced by an equal and opposite rotation, +*a*, of *d*-amyl. "Experimentally," the authors say, "this result is obtained by causing active amyl (*i. e.*, *l*-amyl) bromide to act on racemic sodium amylate. Although one isolates, under these conditions, a mixture of the active oxide and the inactive indivisible oxide, this mixture must act in the polariscope as if the optical effect of one of the two asymmetric carbon atoms had been annulled. We have found, for an ether so prepared: $\alpha_D = +0.25^\circ$ in a 0.5 dm. tube......, so that, according to the principle of algebraic superposition, amyl oxide with two identical active carbon atoms must give a rotation......$\alpha_D = +0.50$......in a 0.5 dm. tube. This point established, we prepared this latter amyl oxide by the action of active amyl bromide on active sodium amylate (both from *l*-amyl alcohol), and, as a matter of fact, this substance, properly purified, gave a rotation $\alpha_D = +0.49^\circ$ in a 0.5 dm. tube."

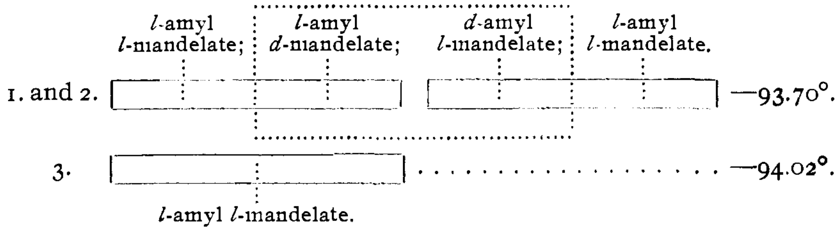
Curiously enough, this result is generally considered as one of the experimental props of the principle of optical superposition. Yet, remembering that one of the two 0.5 dm. tubes contained a mixture, and imagining the ingredients of the mixture as occupying separate halves of that tube, the two polarimetric experiments may be pictured as follows:



Plainly, the rotation in the first tube was one-half that in the second, simply because the first tube contained one-half as much active ether as the second tube. The rotation would still have been one-half if the principle of optical superposition were quite wrong. Assuming the absence of impurities, the slight disparity of the results is due to the fact that in the first tube the active ether was *dissolved* in an equal quantity of inactive ether, the latter having otherwise no more power to counterbalance optical rotation than water or any other inactive solvent.

The rest of Guye and Gautier's observations, and all of Walden's, were made on esters from active alcohols and acids. The theory was that the rotation of an ester with its acid group optically annulled, *plus* the rotation of the ester with its alcohol group optically annulled, must equal the rotation of the ester with neither of its partial rotations annulled, if the principle of optical superposition is correct. Three substances were examined in each case: (1) the ester from an active alcohol and the racemic modification of the acid; (2) the ester from an active acid and the racemic modification of the alcohol; (3) the ester from an active alcohol and an active acid. Thus, to mention one of the many cases investigated by Walden, *l*-amyl *r*-mandelate[1] gave $[\alpha]_D = +2.76°$; *r*-amyl *l*-mandelate gave $[\alpha]_D = -96.46°$. The algebraic sum of the two is —93.70°; and in fact, *l*-amyl *l*-mandelate gave $[\alpha]_D = -94.02°$, the slight difference being attributed to unavoidable impurities.

Now, again imagining the ingredients of the mixtures involved as occupying separate halves of the tubes, the three experiments of this case may be pictured as follows:



Adding the first two results algebraically is equivalent to making a joint observation, as pictured. Since *l*-amyl *d*-mandelate and *d*-amyl *l*-mandelate have equal and opposite rotations,[2]

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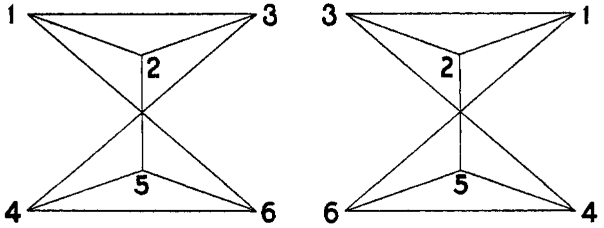
[1] *r* denotes the racemic modification.

[2] That they do have equal and opposite total rotations, whether the partial rotations within each molecule modify one another or not, is obvious from the fact that their molecules are related as an object and its reflected image:



the part of the system enclosed by the dotted lines is optically inactive. But then it is clear that the rotation produced by the first two tubes together equals that produced by the third tube, again not by virtue of the law of optical superposition, but simply because the first two tubes contain together as much active substance (*viz.*, *l*-amyl *l*-mandelate) as the third tube. The slight difference must be due, again, to the solvent influences in the first two tubes.

The cases analyzed above are typical of all the experimental work done in direct connection with the principle of superposition. One further case has been theoretically connected with the principle by Landolt and requires consideration, since different in character from the above. Landolt[1] sees optical superposition in the fact that the molecular rotation of the amyl ester of amylacetic acid equals the molecular rotation of amyl acetate *plus* the molecular rotation of amylacetic acid:

	$[M]_D$.
I. $CH_3COO.C_5H_{11}$	+ 3.25°
II. $C_5H_{11}.CH_2COOH$	+11.08
I+II	+14.33°
III. $C_5H_{11}.CH_2COO.C_5H_{11}$	+14.02

The figures are Walden's. But, on the one hand, using another set of Walden's experimental figures, I find no such agreement in the closely analogous case of the amyl ester of diamylacetic acid:

	$[M]_D$.
I. $CH_3COO.C_5H_{11}$	+ 3.25°
II. $(C_5H_{11})_2.CHCOOH$	+36.54
I+II	+39.79°
III. $(C_5H_{11})_2.CHCOO.C_5H_{11}$	+37.69

On the other hand, cases like Landolt's, if general instead of exceptional, would lead, not to the principle of optical superposition, but to the theorem that the rotatory power of an active radicle is independent of the chemical composition of the rest of the molecule.[2] Indeed, let the rotations of the amyl radicle, when combined with the several groups involved, be respectively as follows:

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[1] "Das optische Drehungsvermögen," 2d ed., p. 267 (Braunschweig, 1898).

[2] Patterson and Taylor (Trans. London Chem. Soc. 87, 33 (1905), seem to think that this is really what is meant by optical superposition.

Amyl with CH_3COO—	*a*
Amyl with —CH_2COOH	*b*
Amyl with $C_5H_{11}CH_2COO$—	*c*
Amyl with —$CH_2COOC_5H_{11}$	*d*

In the case selected by Landolt it happens that $a+b=c+d$, from which he concludes that $a=c$ and $b=d$, *i. e.*, that amyl has the same optical value whether combined with $C_2H_3O_2$ or with $C_7H_{13}O_2$. The error is self-evident.

The accidental equality is readily explained. The reason $a+b$ equals $c+d$ is not that $a=c$ and $b=d$, but that $a<c$ and $b>d$ and the two inequalities nearly balance. Indeed, that the rotation of the amyl group forming esters with fatty acid radicles increases with the mass of the radicles, and is therefore *less* with CH_3COO— than with $C_5H_{11}CH_2COO$—, is shown by the following figures:

Amyl acetate	$[M]_D = 3.25°$
Amyl propionate	3.99
Amyl butyrate	4.25

This points clearly to the inequality $a<c$. On the other hand, the rotation of the amyl radicle of amylacetic acid is known to be *greater* in the acid itself than in its esters; thus,

Amylacetic acid	$[M]_D = 11.08°$
Ethyl amylacetate	10.36,

which points to the inequality $b>d$.

§2. ON VAN'T HOFF'S ASSUMPTION.

It is now clear that all the experimental material hitherto brought forward in support of the principle of superposition really fails to throw any light upon it. And so the question is reopened, is van't Hoff's assumption correct or not?

Before searching for an answer, let us formulate the question itself in lucid terms. An asymmetric carbon atom is a carbon atom linked to four different groups. The numerical value of its rotatory power is well known to depend upon the composition and constitution of each of its four groups. Therefore, the question can only be, is the value of the rotatory power independent of the *stereochemical configuration* of the atoms within each of the four groups?

A negative answer is immediately suggested by the well known fact that the configuration of the maleïc and similar acid radicles has a pronounced influence on the rotatory power of *l*-amyl.

Indeed, when in a given case the maleïnoid configuration is changed to the fumaroid (composition and constitution remaining the same), the rotatory power suffers very considerable change.[1]

	$[M]_D$.		$[M]_D$.
l-amyl maleate	11.82°	*l*-amyl fumarate	15.17°
l-amyl chloromaleate	11.70°	*l*-amyl chlorofumarate	16.78°
l-amyl bromomaleate	15.36°	*l*-amyl bromofumarate	20.07°
l-amyl methylmaleate	11.17°	*l*-amyl methylfumarate	16.01°

In cases like these it may be thought that configuration influences the optical effect because the motion ("free rotation") of the radicles is interfered with by the double bond. And so it may still be asked, is optical effect independent of configuration in the absence of double bonds? The *hypothesis* of optical superposition, as already stated, is nothing but an affirmative answer to this question. But it will presently be seen that *facts* furnish a negative answer; in other words, that facts lead to a proposition which is exactly the reverse of the "principle" of superposition.

The facts in question are the rotatory powers of the *l*-amyl esters of dextro, levo- and meso-tartaric acids, which represent the simplest possible, and hence the most reliable case. Let the principle of superposition be true and the amyl rotation independent of the configurations of the acid radicles, and therefore the same in the three, say a. Similarly, let the independent rotation of the dextro-acid radicle be $+b$, that of the levo-acid radicle $-b$, and that of the meso-radicle *zero*. Then the rotations of the three esters should be:

I. *l*-amyl *d*-tartrate	$a + b$
II. *l*-amyl mesotartrate	$a + 0$
III. *l*-amyl *l*-tartrate	$a - b$,

and the difference between I and II should be the same as that between II and III.

Now III, the rotation of *l*-amyl *l*-tartrate, has never been actually observed. It can, however, be ascertained by a simple and highly reliable calculation; and that, strange to say, from observations made by Walden himself in connection with that erroneous demonstration of the principle of superposition. Indeed, while the experiments of Guye and of Walden fail to test this principle, they do prove that the rotation of, say, a l_1d_2 com-

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[1] Landolt, p. 258. The figures are from Walden: Z. physik. Chem. 20, 377 (1896).

pound may be very closely calculated from the rotations of l_1r_2 and r_1d_2. Theoretically the question might have arisen as to whether the solvent influences involved would not render the algebraic sum of the rotations of l_1r_2 and r_1d_2 considerably different from the rotation of l_1d_2. But Guye's and Walden's numerous experiments prove conclusively that the solvent influences are slight and that algebraic summation yields highly reliable results. Moreover, since the compound r_1d_2 is the mirror-image of r_1l_2, the rotation of the latter may be obtained by reversing the sign of the rotation of r_1d_2. But then, knowing the rotations of l_1r_2 and r_1l_2, we find, by algebraic summation, a value for the rotation of l_1l_2, which is again very close to the truth. Finally, by reversing the signs of the rotations of l_1d_2 and l_1l_2, we obtain the rotations of d_1l_2 and d_1d_2. *In this manner it is easy to calculate quite exactly the rotations of all the combinations possible in a given case if only the rotations of any two of the combinations of active with racemic radicles are known.*

Walden observed:

r-amyl *d*-tartrate..........	$[M]_D = +40.89°$
l-amyl racemate............	$+9.77°$

Reversing the sign of the *d*-tartrate, we have:

r-amyl *l*-tartrate............	$[M]_D = -40.89°$
l-amyl racemate............	$+9.77°$

Two algebraic summations now give:

l-amyl *d*-tartrate............	$[M]_D = +50.66°$
l-amyl *l*-tartrate............	$-31.12°$

For *l*-amyl mesotartrate Walden observed $[M]_D = +13.83°$. And so we have:

I. *l*-amyl *d*-tartrate......	$[M]_D = +50.66°$
II. *l*-amyl mesotartrate..	$+13.83°$
III. *l*-amyl *l*-tartrate	$-31.12°$

The difference between I and II is 36.83; the difference between II and III is 44.95. The considerable disagreement points clearly against van't Hoff's assumption and in favor of a general principle that may be provisionally stated as follows:

The optical rotatory power of an asymmetric carbon atom depends upon the composition, constitution, AND CONFIGURATION *of each of its four groups.*

The same conclusion is reached, in a slightly different way, by comparing the rotations of *l*-amyl mesotartrate and *l*-amyl racemate. Assuming the rotation of the racemate to be very nearly one-half the sum of the rotations of *l*-amyl *d*-tartrate and *l*-amyl *l*-tartrate,[1] the rotations of the racemate and the mesotartrate should be *very nearly* the same if the principle of superposition were correct. In reality Walden found:[2]

l-amyl racemate................	$[M]_D =$	9.77°
l-amyl mesotartrate..........		13.83°

The difference is great.

Less decisive is the case of the *l*-amyl esters of the racemic and meso-modifications of dimethylsuccinic acid.[3] Here the molecular rotations found by Walden are, respectively, 10.47° and 9.79°. The difference, however, which happens to be small, might be due either to the influence of configuration or to extra-molecular influences in the racemate mixture. The point can only be decided by examining the esters of the *d*- and *l*-acids separately.

I am instituting a series of experiments, designed to further test the principle provisionally formulated in this paper, and hope to communicate the results before very long.

It is a pleasure, in concluding, to acknowledge my indebtedness to Professor Morris Loeb, of this University, for a number of important suggestions concerning both the subject-matter of the present paper and its presentation.

DETERMINATION OF THE SODIUM PHOSPHATES.

BY C. CHESTER AHLUM.

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BECAUSE of the close similarity of the reactions of disodium hydrogen phosphate and trisodium phosphate, the quantitative determination of these salts when in mixture requires special and modified methods.

It is known that both of these phosphates may be titrated with standard acid and if isolated may be determined with accuracy by this means. Both disodium hydrogen phosphate and tri-

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[1] This assumption, again, is justified by the very observations that were intended to prove the principle of superposition. It is further justified by the observations of Hammerschmidt (see Landolt: loc. cit. p. 213).

[2] Loc. cit.

[3] Landolt: loc. cit. p. 258.