

XV.—ON THE RELATIONS EXISTING BETWEEN THE PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION OF ORGANIC SUBSTANCES.

[First Paper.]

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For about eighteen months past I have been engaged in investigations on the correlations between the chemical constitution and physical properties of organic substances. At the meeting of the Association for the Advancement of Science (Naturforscherversammlung), at Baden-Baden, of this year (1879), I gave a short account of the results hitherto attained. A detailed paper concerning this subject will shortly appear in *Liebig's Annalen*, and it may, perhaps, be not without interest to the Chemical Society, to communicate, in the following, a condensed account of the contents of the paper in question.

My work has, so far, been restricted to the comparison between the specific gravity and the index of refraction of liquid bodies, and the optical refractive and dispersive properties deduced from these constants.

Among the physical properties of organic compounds, the index of molecular refraction—also called, “the equivalent of refraction”—has already been thoroughly investigated, chiefly by H. Landolt and J. H. Gladstone, and many interesting analogies between these physical properties and the chemical properties of the substances in question, have already been noted.

At the suggestion of Prof. Landolt I decided, therefore, to subject this district, in the first place, to renewed investigation. I communicate in this place only a few of the results that I have obtained by the comparison of the molecular refractive capacities. The results of the comparison of the other constants can be found in the *Annalen*.

The property that matter possesses of refracting light, is one that depends on its chemical composition—the quality and combining proportions of the elements; but it is also closely dependent on the density, so that the denser bodies are, as a rule, the more strongly refractive; it is furthermore dependent on the temperature. Now, we are not able, in the case of liquid (and solid) bodies, to investigate the influence of temperature on the refractive properties separately from that of density, because warming and dilation are correlative

processes, and the expansion of a liquid enclosed in a glass prism cannot well be prevented. For the comparison of the refractive power of these substances with their chemical constitution, it is necessary to use a measure that has been freed from the influence of temperature, and based on equal densities. Through numerous investigations of Gladstone and Dale, Landolt, Wuellner, and others, it has been shown that the index of refraction, diminished by unity, and divided by the density, $\frac{n-1}{d}$, represents for every substance a

value independent of the temperature. It is constant alike for liquid, solid, and even gaseous bodies, so that it may be termed, for all three states of matter, a common measure of the *relative refractive power* or the *specific refractive capacity*.

In the case of substances of low refractive capacity, there may be substituted for n , in the above formula, the index of refraction for light of any particular wave-length (color), *e. g.*, for the red ray of the hydrogen light $H\alpha$, which coincides with the Fraunhofer solar line C. In the case of more strongly refracting bodies, on the contrary, none of the observed indices can be used for the purpose of comparing them in regard to their refractive power, as they are all influenced by dispersion. An index of refraction free from dispersion, is one for a ray of infinitely great wave-length.

If μ_{λ_1} represents the observed index for light of the wave-length λ_1 , and μ_{λ_2} for such of the wave-length λ_2 , we can, as is well known, in the case of not too strongly refractive substances, make, according to Cauchy:

$$\mu_{\lambda_1} = A + \frac{B}{\lambda_1^2}$$

$$\mu_{\lambda_2} = A + \frac{B}{\lambda_2^2}$$

whence follows:

$$B = \frac{\mu_{\lambda_2} - \mu_{\lambda_1}}{\frac{1}{\lambda_1^2} - \frac{1}{\lambda_2^2}}$$

$$A = \mu_{\lambda_1} - \frac{B}{\lambda_1^2}$$

wherein B represents the coefficient of dispersion, and A, the index sought, for a ray of infinitely great wave-length.

This value of A may now be introduced into the formula $\frac{n - 1}{d}$ as the pure coefficient of refraction, independent of dispersion, in the place of the crude index of refraction, n . For each individual substance, the constant: $\frac{A - 1}{d}$ will then be influenced solely by the chemical character, and will be independent of variations in density and dispersion, and also of temperature. This expression can, therefore, be accepted as a true measure for the optical refractive force of the substance.

If these constants be multiplied by the molecular weight, P , of the compounds, then will $P \left(\frac{A - 1}{d} \right)$ be the refractive capacity computed on chemically comparable quantities; hence the molecular refractive capacity, or, as I shall hereafter call it, the *molecular refraction*.

In my experiments, the determinations of density and indices of refraction were always made exactly at 20°. The density was determined with perfect accuracy to the fourth decimal place. I represent this value, compared with water, at 4°, and reduced to vacuo by

$$d \frac{20}{4}$$

The indices of refraction were determined for the sodium light, and for the three light bands of the hydrogen spectrum, by the method of minimal deviation (*kleinster ablenkung*).

The measurements were made with the aid of an excellent spectrometer, by Meyerstein, of Goettingen, which permitted the determination of the indices, with accuracy, to the fourth decimal place, varying by a few units in the fifth place. During the observation, a fine thermometer was kept in the previously-warmed prism, which permitted the temperature to be determined with accuracy to 0.1°.

As a rule, the coefficient of refraction, A , was determined from the indices for the red hydrogen line, H_{α} , and the violet, H_{γ} .

The substances employed were partly prepared by myself, partly obtained from the establishment of C. A. F. Kahlbaum, in Berlin. For the propargyl derivatives mentioned in the following, I am indebted to the courtesy of Mr. Louis Henry, of Loeven.

The greatest care was taken with regard to the purity of the materials employed, which was always tested by analysis.

Through the investigations of other observers, and, especially, through the numerous and carefully elaborated observations of Landolt, it has been proven that isomeric substances behave

similarly in regard to the transmission of light; that only the combining proportions, but not the mode in which the atoms are grouped, is of influence on the molecular refraction. From this it follows that the atoms in all compounds possess the same specific refractive capacity, no matter what the arrangement may be. Landolt has used this fact to determine the refractive power of the atoms from the observed molecular refraction of the compound bodies.

Substances were compared that differed from each other in composition by 1 carbon, 2 hydrogen, or 1 oxygen atom, and the difference in the molecular refractive powers gave directly, therefore, the atomic refraction of the individual elements. In this manner, Landolt obtained the following values, computed on a ray of infinitely great wave-length:

	Atomic Refraction r_A .
C.....	4.86
H.....	1.29
O.....	2.90

With the help of these constants, the molecular refraction of substances containing carbon, hydrogen and oxygen, $C_xH_yO_z$, may now be calculated by the equation: $R_A = 4.86x + 1.29y + 2.90z$; and, in fact, it was shown that the molecular refraction calculated in this manner, agreed, as a rule, very closely with those deduced from actual observation.

The results of these beautiful investigations of Landolt were confirmed, later, by Gladstone, who, by extending the investigation to inorganic substances, showed that in the case of the latter, the rule also holds good, that the molecular refraction is equal to the sum of the atomic refractions.

Later investigations of Gladstone have, however, shown that this law has its exceptions, and it became apparent that the number of these exceptions was, in the case of organic bodies, very considerable.

A series of compounds, belonging to different classes, such as the benzole derivatives, the terpenes, many alkaloids, essential oils and other substances rich in carbon, possess, as Gladstone showed, an exceptional optical behavior. The observed molecular refraction is greater than that computed from the sum of the atoms present therein.

No satisfactory explanation of this peculiarity has hitherto been offered, still less has any attempt been made to show a connection

between the chemical character of these compounds and their apparently abnormal optical properties, which latter are distinct for each class of these substances.

I have succeeded in discovering such a connection. It results, namely, from my investigations, that, under certain conditions, the grouping of the atoms is of essential influence on the molecular refraction of the substance, and that the relations between this physical property and the chemical constitution may be accurately followed out and expressed in simple numbers.

From considerations which need not here be stated, I arrived at the view that, in the so-called unsaturated compounds, those atoms which are repeatedly and directly combined with each other, must exert a greater effect on the transmission of light than those atoms which are combined with each valence to another one.

When, therefore, for instance, hydrogen atoms are subtracted from a hydrocarbon, in such a manner that the exit of each pair of atoms causes a double binding of neighboring carbon atoms, the molecular refraction of the compound becomes greater than that computed from its percentage composition.

If R_A represent the equivalent of refraction, computed from the empirical compositions of such an unsaturated hydrocarbon, a , the influence of a double binding on its molecular refraction, and x , the number of hydrogen atoms removed—therefore, in this case, also the number of the double bindings—, then, according to this view, the molecular refraction of a body of the general formula, $(C_nH_{2n+2}) - xH_2$, should be : $P \left(\frac{A-1}{d} \right) = R_A + x.a$.

Furthermore, according to this hypothesis, the constitution will have no special effect on the optical behavior of unsaturated compounds, in which there exist no multiple attractions between neighboring carbon atoms, but wherein the exit of constituents from the saturated substance, results in a combination of carbon atoms not previously directly combined with each other. Their molecular refraction will correspond to the empirical composition : $P \left(\frac{A-1}{d} \right) = R_A$.

Substances of the formula, $(C_nH_{2n+2}) - xH_2$, in which not only multiple binding between neighboring carbon atoms, but also attraction between remoter carbon atoms, exists, will, therefore, if y be the number of pairs of hydrogen atoms, the elimination of which leads to the formation of a ring-like binding, and hence can have no special influence on the optical properties, possess the molecular refraction :

$$P \left(\frac{A-1}{d} \right) = R_A + (x - y).a.$$

For instance, in hexylene [in general in the olefines of the series $(C_nH_{2n+2}) - H_2$], there is a doubly bound carbon pair. The molecular refraction of this body should therefore be :

$$P \left(\frac{A-1}{d} \right) = R_A + a.$$

In diallyl, a body of the formula $(C_nH_{2n+2}) - 2H_2$, there are two carbon double bindings ; the molecular refraction should therefore be :

$$P \left(\frac{A-1}{d} \right) = R_A + 2a.$$

On the contrary, in benzole, and its derivatives of the formula $(C_nH_{2n+2}) - 4H_2$, a ring-shaped combination of the atoms is assumed, and only three double bindings ; in these bodies, therefore, $x - y = 4 - 1 = 3$, and according to the view previously mentioned, the molecular refraction of these bodies should be :

$$P \left(\frac{A-1}{d} \right) = R_A + 3a.$$

This hypothesis has, in general, been confirmed by experiment. It has become apparent that the refractive power of the atoms, of which the affinity is completely saturated, remains constant, no matter how they may, in other respects, be combined ; that, on the contrary, the atomic refraction is altered by incomplete saturation of the valence.

In this communication, only the influence of the multiple binding between carbon atoms will be considered ; the case of oxygen will form the subject for a future paper.

In the following table, under the heading, "substances with one carbon double binding," are given a number of such substances belonging to several different series:

SUBSTANCES WITH ONE CARBON DOUBLE BINDING.

I.	II.	III. $P \left(\frac{A-1}{d^{\frac{2}{3}} \rho} \right)$	IV. R	V. Diff.
Ethylene perchloride.....	C_2Cl_4	49.7	47.8	+ 1.9
Allyl alcohol.....	C_3H_6O	27.1	25.2	1.9
Acrolein.....	C_3H_4O	25.3	22.6	2.7
Allyl-ethyl ether.....	$C_6H_{10}O$	42.2	40.1	2.1
Allyl acetate.....	$C_6H_8O_2$	42.2	40.4	1.8
Allyl chloride.....	C_3H_5Cl	32.6	30.6	2.0
Methacrylic acid.....	$C_4H_6O_2$	35.1	33.0	2.1
Amylene, 34-35°.....	C_6H_{10}	39.3	37.2	2.1
Mean....				+ 2.1

Column III. contains the molecular refraction found; IV., that calculated by addition of the refractive capacities of the atoms.

In the foregoing calculations of R_A , the following values were employed as the atomic refraction of the elements:

	Atomic Refraction r_A .
C	4.86
H	1.29
O	2.90
Cl	9.53
Br	14.75
N	5.35

of which those for carbon, hydrogen and oxygen, were determined by Landolt; for chlorine and bromine, by Haagen; and for nitrogen, by myself.

Column V. of the table contains the difference between the observed and the calculated molecular refraction: $P\left(\frac{A-1}{d}\right) - R_A$. It will be noticed that these differences are always positive, and that they differ in general very little from the mean + 2.1.* From these numbers we have, therefore, the result that :

The molecular refraction of a substance containing one carbon double binding, is greater by about two than that calculated from the sum of the specific refractive capacities of the constituent atoms.

$$M_A = P\left(\frac{A-1}{d_{20}^0}\right) = R_A + 2.$$

The next table is divided into two compartments. In the upper are given the "substances with two carbon double-bindings." The lower contains a number of "substances with three carbon double bindings," collectively benzole derivatives. The arrangement of the table is the same as in the previous one :

SUBSTANCES WITH TWO CARBON DOUBLE BINDINGS.				
I.	II.	III.	IV.	V.
		$P\left(\frac{A-1}{d_{20}^0}\right)$	R_A	Diff.
Valerylene.....	C_5H_8	38.7	34.6	+ 4.1
Diallyl	C_6H_{10}	46.0	42.1	3.9
Mean....				+ 4:0

* The only notable exception is acrolein, a substance which, as is well known, is difficult to obtain in a state of purity.

SUBSTANCES WITH THREE CARBON DOUBLE BINDINGS.

I.	II.	III.	IV.	V.
		$P \left(\frac{A-1}{d_{\lambda}^2} \right)$	R_A	Diff.
Benzole	C_6H_6	42.2	36.9	+ 5.3
Chlorbenzole	C_6H_5Cl	50.7	45.1	5.6
Brombenzole	C_6H_5Br	55.8	50.4	5.4
Aniline	C_6H_7N	49.8	43.5	6.3
Nitrobenzole	$C_6H_5NO_2$	52.6	46.8	5.8
Toluole	C_7H_8	50.1	44.3	5.8
o-Toluidine	C_7H_9N	57.6	51.0	6.6
Benzyl alcohol	C_7H_8O	53.2	47.2	6.0
Mesitylene	C_9H_{12}	65.8	59.2	6.6
Phenylpropyl alcohol	$C_9H_{12}O$	68.8	62.1	6.7
Hydrocinnamic acid ester	$C_{11}H_{14}O_2$	83.3	77.3	6.0
				Mean . . . + 6.0

As may be seen, the molecular refraction of valerylene and diallyl is about 4 units higher than the sum of the atomic refractions R_A —that is to say:

In the case of substances containing two carbon double bindings, the excess of the actual over the theoretical molecular refraction is twice as great as in the case of substances containing but one pair of doubly bound carbon atoms.

$$M_A = P \left(\frac{A-1}{d_{\lambda}^2} \right) = R_A + 4.$$

In the second compartment of the table, we find the difference between the observed and the calculated molecular refraction to be, in the mean, + 6. The deviations from the mean are, however, somewhat greater here than with bodies with but one or two doubly bound carbon atoms, and greater than could have been caused by errors of experiment. This considerable deviation is due to the fact that the benzole derivatives have a large dispersive capacity. The simple Cauchy's formula, with two constants, that was quite sufficient with substances of not too great refractive capacity, is here inadequate for the complete expression of the dispersion, and it is, therefore, not possible, with the aid of this formula, to determine with perfect accuracy the index of refraction, A , for light of infinite wave-length, in the case of the aromatic compounds. Nevertheless, the variations of the differences from the mean is even here not so great as to conceal the relations previously noted. On the contrary, it follows, from the behavior of the benzole derivatives, that:

Substances containing three carbon double bindings, show an excess of the actual over the calculated molecular refraction, which

amounts to three times that resulting from the influence of a single carbon double binding.

$$M_A = P \left(\frac{A - 1}{d^{\frac{2}{3}} \cdot \frac{2}{3}} \right) = R_A + 6.$$

I have already convinced myself of the fact that the molecular refraction increases with the number of the C=C groups. This is, for instance, the case with the derivatives of cinnamic acid, with methyl-diphenylamine, etc. The dispersion of these, and all very strongly refractive substances, is so great, that Cauchy's formula, with *two* constants, for the determination of the index of refraction, *A*, independently of the wave-lengths, is here no longer applicable. I shall, therefore, be obliged to defer the communication of the results obtained with this material until the completion of the somewhat voluminous calculations, made with the aid of a dispersion formula better in accord with the results of the observations. It is, however, even now, hardly to be doubted that the rule which has, so far, proven to be without exceptions, will also prove to be of general application. The rule, namely, that:

The molecular refraction of substances containing carbon double bindings, is greater than the value calculated from the sum of the atoms, and, especially, the excess is proportioned to the number of such multiple attractions; it amounts to 2 units for one, and 2.z for z double bindings.

$$M_A = P \left(\frac{A - 1}{d^{\frac{2}{3}} \cdot \frac{1}{3}} \right) = R_A + 2.z.$$

We have learned from the preceding statements that the molecular refraction increases by two units for each double carbon binding. The atomic refraction of the carbon in saturated compounds is 4,86; we have, therefore, as the equivalent of refraction of the group C=C:

$$C=C = 2.4,86 + 2 = 11,72.$$

As the attraction of the atoms is reciprocal, each of the carbon atoms in the above group contributes in the same measure with the other to the increase of the molecular refraction. The atomic refraction of a single doubly bound carbon atom is, therefore:

$$C= = \frac{11,72}{2} = 5,86.$$

The atomic refraction of carbon increases, therefore, through the double binding, from 4,86 to 5,86, or to the extent of about 20 per cent. of its original value,

From the facts here communicated, it results: *that the atomic refraction of carbon is not invariable, but that it, on the contrary, varies according to the demands upon the valence of the carbon atom. This has been proven to be the case with oxygen, and it most probably holds true of all the polyvalent elements. The atomic refraction of the univalent elements, whose combining capacity is always completely utilized, must, therefore, be constant, no matter with what atoms they are combined.*

This result is furthermore confirmed by the fact, that in the so-called saturated compounds, in which, consequently, all of the available affinity is utilized, the molecular refraction is independent of the mode of grouping of the atoms, and is determined solely by the combining proportions of the elements.

The chemical constitution of bodies is, therefore, only under certain clearly defined conditions, of essential influence on their optical properties—namely, only then when the available affinity of the atoms of the compound in question does not appear to be entirely utilized. The molecular refraction of such bodies may, however, be determined, *a priori*, if the arrangement of the atoms is known.

The molecular refraction is, then, the sum of the atomic refractions, under employment of the specific refraction peculiar to each atom in the condition in which it is bound in the molecule.

If C' represents the singly bound carbon atoms, and C'' those that are doubly bound to each other, then the molecular refraction of a substance consisting of carbon and hydrogen, C'_xC''_yH_w, results from the sum:

$$M_A = P \left(\frac{A-1}{d_{20}^4} \right) = 4,86x + 5,86y + 1,29w.$$

This law may also be expressed in another, and, for practical employment in calculation, more convenient way, thus:

The molecular refraction of the saturated compounds is independent of the mode of grouping of the atoms; it is, namely, the sum of the atomic refractions:

$$M_A = P \left(\frac{A-1}{d_{20}^4} \right) = 4,86C_x + 1,29H_w = R_A.$$

The molecular refraction of unsaturated bodies is greater than the value calculated from the sum of the atoms, when in such bodies double bindings of the carbon atoms occur, and, especially, the excess amounts to 2 units for one and 2z for z double bindings:

$$M_A = P \left(\frac{A-1}{d_{20}^4} \right) = R_A + 2z.$$

When the analogies were first discovered, which pointed to the optical influence of the multiple bindings of the polyvalent, and especially of the carbon atoms, as the cause of the apparently abnormally high molecular refraction of the so-called unsaturated bodies, the supposition seemed probable that substances containing the acetylene group would show a behavior similar to that of the other unsaturated compounds—namely, that through the elimination of the two hydrogen atoms in the group $-\text{CH}=\text{CH}-$ of the allyl derivatives, the molecular refraction of the products would again increase. I was, therefore, not a little surprised to learn, through experimental investigation, that the removal of the hydrogen produces an entirely different optical effect.

The known derivatives of acetylene are unfortunately neither very numerous nor even, on account of the marked predisposition of these bodies to polymerisation, very easy to prepare in a state of purity and in larger quantities. I must, therefore, restrict myself at present to the communication of the results obtained in the investigation of the propargyl derivatives. Mr. Louis Henry, who has most obligingly aided me in my work, had the kindness to place at my disposal three representatives of this remarkable class of bodies. The observations made on these three substances are given in the following table:

I.	II.	III. $P \left(\frac{A-1}{d^{\frac{3}{4}} \rho} \right)$	IV. R_A	V. Diff.
Propargyl alcohol.....	$\text{C}_3\text{H}_4\text{O}$	24.0	22.6	+ 1.4
Propargyl-ethyl ether.....	$\text{C}_5\text{H}_8\text{O}$	39.5	37.5	2.0
Propargyl acetate.....	$\text{C}_5\text{H}_6\text{O}_2$	39.7	37.8	1.9
				Mean... + 1.8

As may be seen from column V., the difference between the actual and the theoretical molecular refraction, attains in but one case the previously found mean value for the equivalent of refraction of the double carbon binding.

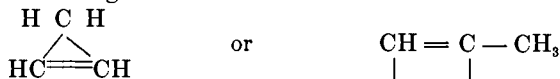
The excess of the observed over the theoretical molecular refraction in the case of the propargyl derivatives, amounts in the mean to 1.8:

$$M_A = P \left(\frac{A-1}{d^{\frac{3}{4}} \rho} \right) = R_A + 1.8.$$

On account of the limited number of the materials for experiment, this expression cannot be claimed to be absolutely exact, and it is, therefore, at present, only to be termed a tolerably close approximation to the truth.

The molecular refraction of the propargyl derivatives is, therefore, greater than that computed from their empirical formulæ. It is, however, remarkable that the elimination of four hydrogen atoms from the corresponding saturated bodies has, in this case, exerted no greater optical influence than a single double carbon binding.

For the present, and as long as more numerous materials for observation are not at hand, the question whether a triple carbon binding is possible or not must remain in abeyance. The optical behavior of the propargyl derivatives would speak against the presence of such binding in these bodies. Their molecular refraction, $M_A = R_A + 1.8$, would be more in accord with the hypothesis of a ring-shaped arrangement of the atoms, or, perhaps, also with that of free valences, so that propargyl hydride, or allylene, would possess one of the following constitution formulæ:



It is apparent that the study of the physical properties is precisely adapted to solve such questions as to the arrangement of the atoms.

In a hydrocarbon of the formula, $(C_n H_{2n+2}) - 4H$, the chemical constitution may, for instance, differ, inasmuch as there may occur therein:

1. Two ring-shaped bindings.
2. One ring-shaped and one double binding.
3. Two double bindings.

The molecular refraction gives us information as to which of the different constitution formulæ is applicable, for in each case the optical behavior is different, and especially, the molecular refraction would be:

1. $M_A = R_A$
2. $M_A = R_A + 2$
3. $M_A = R_A + 4$

In a later paper, I shall have occasion to show how, in fact, the molecular refraction may be used to determine the grouping of the atoms in bodies in which it has hitherto been doubtful or altogether unknown.

In the case of saturated compounds, in which the molecular refraction can give no clue as to the arrangement of the atoms, other physical constants may be employed, and the demonstration of these relations will form the subject of a communication in the near future.

AACHEN, November, 1879.

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