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to two or more liquids, tells us that the electromotive force of any arrangement is equal to the algebraical sum of all the separate differences of potential at the various surfaces of contact of dissimilar substances, each difference of potential being measured by an induction method such as we have described and used. The chemical theory tells us that the energy given out in any electric circuit must be equal to the consumption of chemical energy in the circuit. The electromotive force, then, in any circuit can either be calculated on the contact theory, if we know *each of all* the differences of potential at the various surfaces of separation of dissimilar substances (solid, liquid, or gaseous) in the circuit, or it may be calculated on the chemical theory, if we know exactly what are *all* the physical and chemical changes taking place and the heat-equivalent of every one of them. And the amount of the electromotive force determined in either of these two ways must be identical.

The question of the relative delicacy of the two methods is a totally different question. Any balance accurately made will weigh accurately; but one form of chemical balance is more delicate than another: so, in the same way, there is every reason for believing that an electric test is a far more delicate test of chemical action than the analytical methods employed by the chemist. For example, the action of even small quantities of paraffin-wax on metal, which would quite escape the test of a chemical analysis, we have not only detected, but even measured, with an electrometer*.

VII. *Specific Refraction and Dispersion of Isomeric Bodies.*

By J. H. GLADSTONE, *Ph.D., F.R.S.*†

AMONG the properties of a body which are least liable to change, and which are the most capable of throwing light on its molecular constitution, is its specific refraction. This is the refractive index minus unity divided by the density, or $\frac{\mu-1}{d}$.

In early papers on the subject‡, this specific refraction (or "specific refractive energy," as it was then called) was shown to be a constant, unaffected, or nearly so, by change

* "Contact Theory of Voltaic Action," Part II, by Profs. W. E. Ayrton and John Perry, Proc. Roy. Soc. No. 186, pp. 26-34, 1878.

† Communicated by the Physical Society, having been read at the Meeting on November 27, 1880.

‡ Phil. Trans. 1863, p. 323, and 1869, p. 9; Journ. Chem. Soc. 1865, p. 108; Landolt, Pogg. *Ann.* cxxii. p. 545; Wüllner, *ibid.* cxxxiii. p. 1.

of temperature, by the passage from the liquid to the solid or even gaseous condition, by mixture with other liquids, or by solution, or even (within certain limits) by changes of chemical combination.

In regard to changes of temperature, however, it was observed at the very commencement that there was "some influence, arising wholly or partially from dispersion,"* which interferes with the exactitude of the law. In order to obviate this, if possible, the calculations were made for the least-refrangible limit of the spectrum, according to the formula of Cauchy. But it was found that these gave results little, if at all, more exact than those for the line A of the solar spectrum. In our subsequent work, Mr. Dale and I did not consider it worth while to go through the labour of this calculation; and my observations are always reckoned, if possible, for the line A, whilst Landolt has preferred the α of hydrogen gas, which is identical with the solar line C.

In regard to the passage from one state of aggregation to another, the few cases that have been directly observed are fairly in accordance with the law †.

In the case of mixtures of liquids ‡, the conclusion that the specific refraction of a mixture of liquids is the mean of the specific refractions of its constituents is a near approximation, if not an absolute truth.

With regard to the influence of solution, some doubt has recently been thrown upon the deductions drawn from dissolved salts or other chemical compounds; but the general, if not absolute, correctness of the method is supported by a very large amount both of direct proof and collateral evidence §. As an instance of the latter, I may quote the last observations made in my laboratory. The specific refraction of pyrene, $C_{16}H_{10}$, as determined from its solution in benzol, in chloroform, and in carbon disulphide, is respectively

$$\cdot 6235, \quad \cdot 6252, \quad \cdot 6240,$$

a practical agreement which could scarcely happen if the method were erroneous. Taking the mean of these numbers, and multiplying it by the atomic weight, we obtain, as the refraction-equivalent of pyrene, the very high figure of 126.1.

In regard to chemical combination, it is now well understood that an elementary substance such as carbon will exert the same retarding influence upon the rays of light throughout

* Phil. Trans. 1863, p. 323.

† Phil. Trans. 1869, pp. 10, 11.

‡ Phil. Trans. 1863, p. 332; Landolt, *Ann. Chem. Pharm.* iv. (Sup. Bd.) 1865, p. 1.

§ Phil. Trans. 1869, pp. 14, 15.

a very large number of its compounds, whilst in others it may exert a different influence. This has naturally attracted the attention of organic chemists to the subject, and promises to be a very fruitful field of investigation.

In the present communication I intend to confine my remarks to those groups of bodies which exhibit isomerism. It is well known that two or more compound bodies, differing from one another in physical or chemical properties, may be composed of the same elements in precisely the same proportions. In such a case the specific refraction may be the same, or it may be different.

It is found to be the same notwithstanding differences of other optical properties, differences of molecular weight, and differences of chemical properties.

1st. *Differences of other optical properties.*—It so happens that among the bodies which display the phenomena of circular polarization, there are several isomeric groups, and that different members of these groups differ from one another in their effect on the polarized ray. Thus with respect to the different terpenes, $C_{10}H_{16}$, some of them rotate the plane of polarization to the right and others to the left, and that to different degrees; yet they have all practically the same specific refraction, 0.537*.

It was also an early observation that solutions of cane-, grape-, and honey-sugar, and gum, of the same strength, though they differ largely in their effect on polarized light, give the same, or very nearly the same, refraction and dispersion†.

Again, it is well known that tartaric acid is an optically active substance, and racemic acid optically inactive, while their chemical composition, $C_4H_6O_6$, is identical. The following table gives the specific refraction and dispersion of these two acids in solution as deduced from data previously published‡. The specific dispersion is the difference between the specific refraction for the line A and that for the line H,

or, which is the same thing, $\frac{\mu_H - \mu_A}{d}$.

	Specific refraction.	Specific dispersion.
Tartaric acid.....	.3020	.0131
Racemic acid.....	.3036	.0143

Carvol and menthol, the odorous principles of caraway and

* Chem. Soc. Journ. 1864, p. 18.

† Phil. Trans. 1863, p. 332.

‡ Ibid. 1869, p. 30.

mint respectively, are very definite substances, of the composition $C_{10}H_{14}O$; but the first rotates the plane of polarization very powerfully to the right, and menthol very powerfully to the left; yet they have practically the same specific refraction*.

	Specific gravity.	Specific refraction.	Specific dispersion.
Carvol from caraway	0.9530	.5126	.0362
” from dill	0.9562	.5115	.0348
Menthol.....	0.9394	.5100	.0331

2nd. *Differences of molecular weight.*—Interesting cases of this are to be found among the essential oils, as shown in the subjoined table, in which the numbers given for the *terpenes* are the mean of ten different specimens, for the *citrenes* of twelve specimens, and for the *cedrenes* of eight specimens, each group probably consisting of several isomerides †.

	Specific gravity.	Specific refraction.	Specific dispersion.	Refraction-equivalent.
Terpenes, $C_{10}H_{16}$	0.8600	.5370	.0302	73.03
Citrenes, $C_{10}H_{16}$	0.8466	.5475	.0336	74.46
Cedrenes, $C_{15}H_{24}$	0.9166	.5392	.0307	110.00
Colophene, $C_{20}H_{32}$	0.9391	.5413	.0329	147.23

The terpenes and citrenes show a constant though not a large difference in specific refraction; but the polymeric bodies of the same series seem to have so nearly the same specific refraction as the terpenes that the differences may be attributed to impurities or experimental error. The refraction-equivalents of the three groups are of course very nearly in the proportions of 2, 3, and 4.

3rd. *Differences of chemical properties.*—In the cases already mentioned it is possible that the differences of physical properties depend upon some difference in the arrangement of the ultimate atoms; but there are other cases in which this is perfectly well known to be the case. Isomeric bodies of this nature are more strictly termed metameric. Delffs showed, as far back as 1850†, that such pairs as formic ether and acetate of methyl, both of the ultimate composition $C_3H_6O_2$, had the same refraction; whilst the papers of Landolt, and the more recent ones of Brühl§, abound in instances. Among the observations in my notebook, hitherto unpublished, occur the following:—

* Chem. Soc. Journ. 1872, p. 9.

† Pogg. Ann. lxxxi. p. 470.

‡ Chem. Soc. Journ. 1864, p. 18.

§ Liebig's Ann. cciii. pp. 1, 255.

		Specific refraction.	Specific dispersion.
Propyl iodide,	C_3H_7I	·2844*	·0216
Isopropyl iodide,	"	·2883*	
Cresol from thymol,	C_7H_8O	·5116	·0454
Metacresol,	"	·5091	·0452
Benzyl alcohol,	"	·5069	·0415
Nitrobenzoic acid (α),	$C_7H_5(NO_2)O_2$	·3994	
" "	(β), "	·4004	
Benzyl butyrate,	$C_{11}H_{14}O_2$	·4777	·0332
" isobutyrate,	"	·4805	·0331
Monochloro-toluol,	C_7H_7Cl	·4807	·0409
Benzyl chloride,	"	·4836	·0409

Though identity of ultimate composition will generally produce identity of specific refraction, there are certain cases in which isomeric (or, rather, metameric) bodies differ widely in their power of retarding the transmitted ray. The earliest of those observed was the case of aniline and picoline, C_6H_7N ; and as Dr. Thorpe has kindly lent me his specimen of picoline, I am able to confirm the previous determinations.

	Specific refraction.	Specific dispersion.
Aniline	·550	·0635
Picoline (<i>C. G. Williams</i>) ...	·513	·0448
" (<i>Thorpe</i>)	·522	·0431

The difference in this pair was originally attributed to the fact that the two bodies "are constructed very differently;" and in subsequent papers it was pointed out that, when the atoms of carbon were not saturated in the usual way, there is an augmentation in their refractive power, analogous to what happens when an element such as iron changes its valency †. Brühl has expressed this more definitely by putting forward the theory that, whenever two carbon atoms are doubly linked, there is an increase of the refraction-equivalent amounting to 2·0 for the limit of the spectrum, as reckoned by Cauchy's formula, or about 2·2 for the hydrogen-line α , and of course a little less than 2·2 for the line A. I have no doubt that both Brühl himself and other chemists will have much to say in the future as to the extent to which this theory may be in accordance with present views of the constitution of the various organic compounds.

* Brühl gives the values 0·2873 and 0·2907 respectively for the line C.
 † Phil. Trans. 1863, p. 333; Chem. Soc. Journ. 1870, p. 150; Proc. Royal Instit. March 1877.

In my notebook I find the following instances of isomeric bodies which differ in specific refraction :—

		Specific refraction.	Specific dispersion.	Refraction-equivalents.
Acetone,	C_3H_6O	·4420	·0207	25·64
Butyric ether,	$C_6H_{12}O_2$	·4402	·0191	51·06
Allyl alcohol,	C_3H_6O	·4734	·0275	27·45
Carvol,	$C_{10}H_{14}O$	·5122	·0355	76·83
Thymol,	„.....	·5206	78·09
Nitraniline (α),	$C_6H_5(NO_2)N$	·469	64·72
„ (β),	„	·546	75·34
Cresylic acetate,	$C_9H_{10}O_2$	·4677	·0348	70·15
Benzyllic acetate,	„.....	·4945	·0394	74·17
Phenyl-ethyl acetate,	$C_{10}H_{12}O_2$	·4776	78·32
Hydrocinnamene acetate,	„.....	·5183	·0382	85·00

Acetone and allylic alcohol have been compared already by Brühl, with similar results, and form one of the striking cases on which his theory depends. The refraction-equivalent of thymol being 6·8 above the normal, is confirmatory of the position which is now given to it in the great aromatic group—a position which I was disposed to assign to it ten years ago, on the evidence of its optical properties.

The two nitranilines were lent to me by Dr. Mills. Unfortunately they are very sparingly soluble bodies; and the above figures, though each of them the mean of three observations, are only given as approximately correct. But that they are really different there can be no doubt.

The two pairs of acetates were lent by Dr. Hodgkinson; and the last one is of particular interest, on account of the cinnamene compound having a higher refraction-equivalent than can be accounted for by any existing theory.

Specific Dispersion.

Though there are several sources of error in determining indices of refraction for the line A or for the line H, the actual distance between these two may be measured with great exactness, and the experimental error rarely, I believe, exceeds 0·0002. The possible error in the determination of the density at the same temperature has also to be considered with regard to specific dispersion; but any inaccuracy in the figures above given will certainly be confined to the fourth place of decimals.

Among the conclusions that may be drawn in regard to dispersion are the two following :—

1st. Where the carbon atoms are exerting a more than normal influence on the refraction of the rays of light, there is

a great increase of dispersion. It was pointed out some years ago that the aromatic bodies have a great dispersive power*, and that "dispersion, as well as refraction, increases very rapidly with the number of atoms of carbon that are not combined with at least two of hydrogen or their equivalent."† Evidence of this is to be found both in the older and the more recent researches, whether in this country or on the Continent, and is always accumulating. Confining our attention to the figures given in this paper, it will be observed that in cases where the carbon is normal the specific dispersion is expressed by low figures (the highest of which is, in fact, acetone, ·0207); while in the isomeric allylic alcohol, which has a higher refraction, it rises at once to ·0275. The essential oils and their congeners, and such bodies as cresylic acetate, are above ·0300; while the purely aromatic compounds are all above ·0400.

2nd. Where isomeric bodies have the same or nearly the same specific refraction for the line A, they have the same also for the line H. The apparent deviations from this rule I am disposed to attribute to experimental error, and still more to impurity of substance. It is clear that in many cases of carbon compounds the presence of a differently constituted body would reveal itself by its influence upon dispersion more than upon refraction.

VIII. *On the Specific Volumes of Oxides.* By BOHUSLAV BRAUNER, *Ph.D.*, and JOHN I. WATTS, *Owens College*‡.

THE researches of Persoz, Karsten, Filhol, Kopp, Schröder, Löwig, Schafarik, Playfair and Joule, Baudrimont, Heimroth, and others have yielded a considerable supply of material relating to the specific volumes of many bodies, especially to those of the oxygen compounds; and by aid of these results many interesting theories can be conceived. It was, however, Kremer§ who first pointed out the regularities which the volumes of the oxides of the natural groups of elements exhibit. But after the demonstration of the Periodic Law by Mendelejeff this question considerably developed in importance, because the relations of the various members of the natural groups to one another were made more strikingly apparent. Mendelejeff himself|| points out the regularities which the specific volumes of the oxides exhibit in the different groups of the system; but he only followed this out in one

* Journ. Chem. Soc. 1870.

† Proc. Roy. Inst. March 1877

‡ Communicated by the Authors.

§ Pogg. Ann. cxxx. p. 77.

|| *Ann. Chem. Pharm.* Suppl. viii. p. 143; *Chem. News*, xl. p. 255, xli p. 49.