

XXIII.—*On the Specific Refractive Energy of Elements and their Compounds.*

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IN February, 1863, the Rev. T. Pelham Dale and I sent to the Royal Society an account of some researches on the Refraction, Dispersion, and Sensitiveness of Liquids, which appears in the Philosophical Transactions for that year, pp. 317-343. We followed this up in the autumn by reading a paper at the meeting of the British Association at Newcastle, an abstract of which is to be found both in the Report of the Association itself, and in *Les Mondes*. In these two communications we showed the high importance of considering what we term the "specific refractive energy," that is, the refractive index minus unity divided by the density, or, in mathematical language, $\frac{\mu - 1}{d}$. Contem-

poraneously with our researches, Landolt was examining the same subject, and in a paper published in the last December number of Poggendorff's *Annalen*, he shows his familiarity with our paper in the *Philosophical Transactions*, and his ignorance of the abstract in the *British Association Report*. He gives much additional proof of the specific refractive energy being a real physical property of bodies, and has advanced the subject considerably in his attempt to show the influence of the atomic constitution of fluid compounds of carbon, hydrogen, and oxygen on the propagation of light.

In the original words of Mr. Dale and myself, "Every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when mixed with other liquids." This proposition may be extended to gaseous and solid bodies, the changes of temperature including those which affect the aggregate condition of the body, and the idea of mixture being enlarged so as to include ordinary cases of solution. Yet this general statement must be taken with a certain reserve. The influence of dispersion and, perhaps, other things, make the expression $\frac{\mu - 1}{d}$ rather an approximation to the truth than the truth itself; and our knowledge of the extent to which chemical combination may modify the specific refractive energies of the elements is as yet very limited.

Temperature.—That the influence of heat on the refraction of bodies is due to its altering their density, and that the specific refractive energy is the same, or very nearly the same, at all temperatures, was shown in our communications to the Royal Society; but it has received confirmation from the careful observations of Landolt on propionic acid, ethylic and amylic alcohols, aldehyde, and hydride of benzoyl.

That this law holds good notwithstanding the passage from the liquid to the solid state is apparent from the observations on water and phosphorus, in previous papers by Mr. Dale and myself;* and we have more recently measured the refractive index of sulphur at the melting point, or rather at the point when crystals began to form in the sulphur previously melted in our prism. The indices of four different parts of the spectrum were as follows:—

* *Phil. Trans.*, 1858, p. 890, and *Phil. Mag.*, July, 1859.

Line A.	Line D.	Line E.	Most refrangible limit.
1·9024	1·9295	1·9527	2·0065

The density of sulphur at this temperature was found to be 1·8063, which gives ·51 as the specific refractive energy for the line D. The refractive index of native sulphur at the ordinary temperature is stated by different observers to be 1·958, 2·008, 2·04, and 2·115, of which the mean is 2·03. The density is said to be 2·04. The specific refractive index of solid sulphur may, therefore, be taken at ·50 for the brightest part of the visible spectrum, a result coincident with that of ·51 for the line D as seen through melted sulphur, at least within the limits of experimental error.

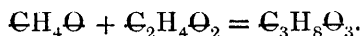
No experiments have been made by us on the refraction of gases, but the observations of Dulong on the vapours of water, bisulphide of carbon, and ether, and of Le Roux on the vapours of phosphorus and sulphur, afford the means of comparing the specific refractive energies of these substances when in a liquid and a gaseous condition. The results are given below, but, as a correction has been made of what appears to be an omission in Le Roux's method of calculation, a query is appended to the determinations of gaseous phosphorus and sulphur.

Condition.	Water.	Phosphorus.	Sulphur.	Bisulph. Carbon.	Ether.
Solid	·336	·58	·50	—	—
Liquid.....	·333	·59	·51	·49	·49
Gaseous	·321	·50?	·49?	·44	·46

From this table it would appear that while the specific refractive energy is the same in the solid and liquid condition, it is somewhat smaller in the gaseous. The differences may disappear on more close examination, but there seems reason to think, from the care that Dulong bestowed upon the matter, that, in reference to water at least, the difference is real.

Mixture and Solution.—With reference to mixture, the following was the conclusion arrived at by Mr. Dale and myself:—"The hypothesis that the specific refractive energy of a mixture of liquids is the mean of the specific refractive energies of its con-

stituents must stand as the nearest approximation to the truth." Landolt has confirmed this in a novel and interesting manner, by taking two organic liquids in certain equivalent proportions, mixing them, and comparing the specific refractive energy of the mixture with that of some organic liquid of the same ultimate atomic composition. He finds in seven recorded instances that the numbers are nearly identical, the refractive energy of the mixture being, however, always very slightly in excess. The most remarkable instance, perhaps, is that of a mixture of single equivalents of methylic alcohol and acetic acid, as compared with glycerin :



The following table of the refractive indices of alcohol of various strengths at 20° C. will serve to illustrate the effect of mixture, and all the better as a considerable contraction ensues, as is well known, on mixing alcohol with water :—

Liquid.		Density.	Refr. Index for A.	Spec. refr. energy.	Calculated mean.
Alcohol.	Water.				
100 parts	0·797	1·3578	·448	—
90 " + 10 parts	0·818	1·3593	·439	·436
50 " + 50 "	0·915	1·3560	·389	·388
25 " + 75 "	0·963	1·3455	·358	·358
	100	1	1·3285	·328	—

The numbers found by observation are as close to those deduced from theory as can be expected in experiments of this nature.

If a substance, in passing from a solid to a liquid state, does not change its specific refractive energy, it is to be expected that the laws of mixture will hold good equally whether both substances were originally liquid, or whether one of them was solid but had been liquefied by solution. And actual observation proves that this is the case. A solid substance when dissolved is found to have the same (or very nearly the same) specific refractive energy as it had previously ; or, to speak more accurately, the specific refractive energy of a solution is the mean of the specific refractive energies of the solvent and the substance dissolved. The following table of solutions of sugar at 20 C. will illustrate this. The refractive index of crystallised cane-sugar is given on the authority of Brewster, its specific gravity on that of Thomson :—

Substance.		Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Sugar.	Water.				
Whole	1·563	1·545	·349	—
66·6 parts + 33·3 parts	1·325	1·455	·343	·344
50 „ + 50 „	1·232	1·418	·339	·341
25 „ + 75 „	1·116	1·377	·337	·337
	Whole	1	1·333	·333	—

This, however, is much more striking where there is a wide difference between the specific refractive energy of the solvent and that of the body dissolved. I became the possessor of a beautiful prism of rock-salt from Mr. J. G. Hofmann's case at the International Exhibition of 1862. Its refractive indices for the three principal lines of the spectrum were found to be—

A.	D.	H.
1·5369	1·5443	1·5685

Newton gave for rock-salt the index 1·545, Brewster 1·557. The refraction of pure chloride of sodium in a solid condition may be assumed as identical, or very nearly identical, with this; hence a solution was made of the chloride in three times its weight of water, and the refractive indices were taken. The following comparison will show that the salt in dissolving retains its original specific refractive energy :—

Substance.	Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Salt	2·086	1·544	·261	—
Solution	1·183	1·377	·318	·315
Water	1·	1·333	·333	—

The idea of solution need not be confined to the liquefaction of a solid. A gaseous body may carry its original specific refractive energy into its combinations with water; and that it sometimes does so (at least, within limits of possible experimental errors) is shown by the following observation on two solutions of ammonia, containing respectively 29·2 and 17·4 per cent. of the alkali. The observations on the gas are given on the authority of Dulong.

Substance.	Density.	Refr. Index for D.	Spec. refr. energy.	Calculated mean.
Ammonia gas.....	0·00076	1·000385	·506	—
Solution, 29·2 p. c.....	0·8863	1·3491	·393	·383
„ 17·4 p. c.....	0·9338	1·3418	·366	·363
Water	1	1·333	·333	—

These instances might be multiplied from observations made by Mr. Dale and myself, and the refractive indices given by A. and E. Weiss* afford the means of similar calculations. The general result is that, as a rule, when a gas, liquid, or solid dissolves in water, it preserves its specific refractive energy; but that there are certain cases—as sulphuric acid—where the departure from what theory requires is too great to be attributed to errors of observation. There is one conclusion which is pretty safe, and may be of great value in future researches. When the refractive index of a strong solution is known, the refractive index of a more dilute solution may easily be reckoned from it, by making the proper allowance for the quantity of water added.

Chemical Combination.—Many of these cases of mixture or solution can scarcely be looked upon otherwise than as feeble chemical combinations. It might fairly be expected that the law which holds good with them would equally apply to some of those simpler combinations of elements, in which the physical properties of the compound do not differ very widely from those of its constituents united. It becomes indeed an interesting question to ascertain how far an element carries into its compounds its specific influence on the velocity of the rays of light.

The simplest cases of combination are where two elements combine, and do not change their aggregate condition, two gases for instance forming a compound gas, or two liquids a compound liquid. In regard to gases, the question was examined some time ago by Dulong, and, from a consideration of nine cases, he came to the conclusion that the refractive power of a gaseous compound is not the sum of the refractive powers of its gaseous constituents. He found it sometimes more, sometimes less; but after all the differences were not very large. It will be observed that Dulong did not compare the specific refractive energies $\frac{\mu - 1}{d}$, but what Newton

* Sitzungsberichte kais Akad. Wissensch. Math. Nat. 1858. xxxiii, 589.

termed the absolute refractive powers $\frac{\mu^2 - 1}{d}$; but though the difference between these formulæ is notable enough when they are applied to liquids or solids, they come to the same thing in the case of gases. This will be apparent from the following considerations:—

$$\mu^2 - 1 = (\mu - 1) \cdot (\mu + 1);$$

now, in a gas, μ consists of 1 followed by three zeros, as 1·000385; $\mu + 1$ therefore becomes a number scarcely exceeding 2, and the above equation amounts practically to

$$\mu^2 - 1 = 2(\mu - 1),$$

and the specific refractive energies of gases are simply half of their absolute refractive powers. Where, however, μ is such a number as 1·385, there is no such constant relation.

In calculating the theoretical specific refractive energy of a compound, it is necessary to multiply the energy of each constituent by the quantity of that constituent, add together the numbers so obtained, and divide the same by the quantity of the whole compound. But it is more convenient to adopt with Landolt what he terms the “molecular refractive energy,” or “refraction-equivalent,” that is, the specific refractive energy multiplied by the atomic weight, or $P\left(\frac{\mu - 1}{d}\right)$. Thus Dulong determined the refractive index (μ) of oxygen as 1·000272; and its specific gravity (d), on the scale of water being 1, is 0·00143. The specific refractive energy $\left(\frac{\mu - 1}{d}\right)$ is therefore ·190; and the refraction-equivalent is $\cdot 190 \times 16$, or 3·04. The refraction-equivalent of hydrogen gas, calculated from his numbers, is 1·53. Hence

	Refr. equiv.
2 atoms of hydrogen	3·06
1 atom of oxygen	3·04
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Sum	6·10

while the refractive equivalent of steam, calculated from Dulong's observations, is only 5·78. Before passing to another compound we may compare these numbers with the refraction-equivalents of

liquid and solid water, as deduced from their specific refractive energies given above :—

	Refr. equiv.
Sum of gases	6·10
Steam	5·78
Water	5·99
Ice.....	6·05

In our paper before the British Association, Mr. Dale and I gave the calculated and observed specific refractive energies of five liquid compounds, but the data were not published. One of these was terbromide of phosphorus, a liquid composed of two elements of which we had determined the refractive indices in the liquid condition.

Bromine permits only the extreme red rays to pass, but the lines A and B of the solar spectrum were perfectly visible, and the following determinations were made :—

	Line A.	Line B.
At 26° C.	1·6243	1·6333
At 35° C.	1·6150	1·6230

which would give for the refractive index of A at 20° C about 1·630; and taking the specific gravity of bromine at 2·98, we have

Specific refractive energy....	·212
Refraction-equivalent	16·9

The refraction-equivalent of melted phosphorus, reckoned from numbers previously given, is 18·3. We have therefore

	Refr. equiv.
1 atom of phosphorus.....	18·3
3 atoms of bromine.....	50·7
Sum	69·0

while the refraction-equivalent deduced from our observations on terbromide of phosphorus itself was only 63·4.

In bisulphide of carbon we have two elements solid at the ordinary temperature combining to form a liquid. The refraction-equivalent of carbon, as obtained from the diamond, is about 5·1 for the most luminous part of the spectrum: that of sulphur may

be taken at $\cdot 50 \times 32$, or $16\cdot 0$ for the line D. We have therefore

	Refr. equiv.
1 atom of carbon.....	5·1
2 atoms of sulphur	32·0
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Sum.....	37·1

The refraction-equivalent reckoned from the actual observations of bisulphide of carbon is $37\cdot 3$ —a very much nearer result than in the two cases previously discussed; indeed the numbers may be considered in this case as identical.

On comparing homologous series, Mr. Dale and I found that every increment of CH_2 caused an increase in the specific refractive energy (except in the case of the hydrocarbons), and we noticed that the amount of optical change was less between the higher than between the lower members of the series. Landolt shows that when the refraction-equivalents are compared, the difference is the same between each two consecutive members, and this difference he finds on an average to be $7\cdot 6$. The actual numbers vary from $6\cdot 81$ to $7\cdot 88$, and the series he compared were the $\text{C}_n\text{H}_{2n}\text{O}_2$ acids, the alcohols, and certain compound ethers. On applying this mode of calculation to the series given in our previous paper, Landolt's conclusion is abundantly confirmed, not only in series commencing with iodide of methyl, formic ether, mercuric methyl, and hydride of œnanthyl, but also in the benzole and pyridine groups. The refraction-equivalent of olefiant gas, C_2H_4 , reckoned from Dulong's numbers, is $15\cdot 09$, which will give for the half CH_2 , $7\cdot 54$.

Landolt, by comparing the refraction-equivalents of liquids differing by a single atom of carbon, by two of hydrogen, or by one of oxygen, is able to show the influence which each of these elements exerts in their compounds, and by taking the following as the refraction-equivalents,

Carbon	=	5·0
Hydrogen	=	1·3
Oxygen	=	3·0

he is able to show a wonderfully close analogy between the calculated and the observed refraction-equivalents of a large number of liquids, all belonging, however, to the same class of organic com-

pounds, with indices ranging only from 1.328 to 1.471. The calculations given above from bisulphide of carbon and olefiant gas, and others that I have made from carbonic acid, the essential oils, and other substances, show the general uniformity of the action of the atoms of carbon on the rays of light, whether these atoms are crystallized together in the form of diamond, or are compounded with oxygen or hydrogen, sulphur or chlorine.

This mode of investigation may be applied to all the elements, and we have so applied it to a considerable number; but it would be premature to publish results, many of which rest on imperfect data. Some of the numbers which are given in this paper will probably have to be corrected. To determine the extent to which chemical combination may modify the specific refractive energies of the elements, and to ascertain the real value of these constants, requires that the refractive index and the density should be taken from the same specimen, that its purity should be guaranteed, that the part of the spectrum measured should be noted, and that the temperature should be mentioned, requisites not usually to be found in the recorded observations of refractive indices.
