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VI. *On the Upper Limit of Refraction in Selenium and Bromine.*

By Rev. T. PELHAM DALE, M.A.*

IN my former paper read before the Society† I showed that the value of the limit could be found by the solution of the equation

$$a \sin \theta = \sin m\theta ;$$

where a is the ratio of wave-lengths in free æther, and $\theta = \frac{\pi h}{l}$, h being what I there called the molecular distance, and l the corresponding wave-length within the medium. If $a \sin \theta$ be greater than unity, the solution is imaginary.

It was also shown that if ν be limit of refraction, μ the index corresponding to θ , that

$$\frac{\mu \sin \theta}{\theta} = \nu.$$

If $\theta = \frac{\pi}{2}$, we have

$$\mu = \frac{\pi}{2} \nu ;$$

μ being the index of the limit of refraction towards the violet end of the spectrum. Call this the upper limit, and denote it by μ_k .

∴ $\mu_k - \nu$ is the total dispersion

$$\text{also} \quad = \left(\frac{\pi}{2} - 1 \right) \nu ;$$

$$\frac{\mu_k - 1}{d} = \text{constant independent of temperature.}$$

Also by the relation

$$\frac{\pi h}{l} = \theta,$$

we have for l_k the upper limit

$$\frac{\pi h}{l_k} = \frac{\pi}{2},$$

or

$$2h = l_k.$$

Hence the quantity h is half the wave-length within the medium of the limiting transmissible ray.

* Read November 10, 1888.

† Proc. Phys. Soc. vol. ix. p. 167.

As also

$$\sin \theta = \frac{\lambda}{\lambda_1} \sin \theta_1,$$

or

$$\frac{\lambda}{\lambda_1} = a,$$

we have at the limit

$$\begin{aligned} \frac{\lambda}{\lambda_k} \sin \theta &= \sin m\theta, \\ &= \sin \frac{\pi}{2} = 1; \end{aligned}$$

$$\therefore \lambda \sin \theta = \lambda_k.$$

If on further examination this upper limit should be established as a physical entity it will modify our ideas of dispersion, which we must then regard as identical with refraction.

There is a relation between the Eulerian integral $\Gamma(n)$ and $\frac{\sin \theta}{\theta}$ which is worthy of notice,

$$n\pi = \theta.$$

By a well-known relation,

$$\Gamma n \cdot \Gamma 1 - n = \frac{\pi}{\sin n\pi}.$$

Hence

$$\Gamma(1+n)\Gamma(1-n) = \frac{n\pi}{\sin n\pi}.$$

If a table of $\Gamma(1+n)$ is at hand, it can be used as a practically expeditious method of finding the value denoted by θ^* .

Also if for n we write $1-n$ in the above, we have

$$\Gamma(1+1-n)(\Gamma 1 - (1-n)) = \frac{\pi - n\pi}{\sin(\pi - n\pi)},$$

or

$$\frac{1-n}{n} \Gamma(1+n) \Gamma(1-n) = \frac{\pi - \theta}{\sin(\pi - \theta)},$$

which gives us

$$\frac{\sin(\pi - \theta)}{\pi - \theta} = \frac{n}{1-n} \cdot \frac{\sin \theta}{\theta}.$$

Now since $\sin(\pi - \theta)$ is equally a solution of the equation, $a \sin \theta = \sin m\theta$, it is probable therefore that this solution may have a physical meaning.

* The tables of logarithms by Vassal containing a column of circular measures of arc serve every purpose as far as calculation is concerned.

It was noticed in my former paper that, of the substances for which data were at hand, selenium alone had its upper limit within the visible spectrum. Accordingly a fresh calculation of the values of θ_k , ν , and λ_k were made and the results given below (Table I.).

It will be seen from the table that the limiting wave-length which is transmissible is $\lambda = 5295.7$. This is a little below λ_E , which is 5269.13. It was of great interest to observe how far this purely theoretical result would be supported by observation. As neither temperature nor specific gravity of specimen were given, and the indices of refraction to the third place of decimals only, it was evident that, as a preliminary experiment, all that could be sought for was a general agreement.

With this in view I had a Browning amateur spectroscopy-eyepiece fitted to my microscope, an old instrument constructed many years ago by Troughton and Sims. After a few trials I succeeded in obtaining a tolerably uniform film of selenium mounted as an ordinary microscope-slide. The film when cold was quite transparent, and transmitted a deep ruby tint. This film was found under the spectroscopy to transmit rays nearly to the line D. Another and thinner slide was prepared. Under the microscope the thinner portions were found to be of a more orange tint, due to a spectrum reaching to the beginning of the green. Even in brilliant sunlight no sensible extension beyond this took place. In parts of the film were holes. If these were in the field they appeared as spectra extending to the violet end, but with sharp well-defined sides, showing apparently that a very thin film was effective to stop all the upper rays. Thus, then, the agreement of theory and observation seems as satisfactory as could be anticipated, considering both the data and instrumental means employed.

The examination of sulphur gave similar results. Here the limiting wave-length lies beyond the visible spectrum. A film of melted sulphur transmits yellow light. This film darkens rapidly as the temperature rises, and when the sulphur begins to boil, it, as is well known, assumes a brownish tint. Examined under the spectro-microscope, it is seen that the absorption is confined to the violet end. If the film be

placed boiling under the spectro-microscope, the spectrum is seen to be generally darkened till near the red end, and the violet quite cut off. As the film cools, the resulting dark cloud seems to recede towards the violet. If the film be very thin it appears colourless to the eye, and under the spectro-scope the violet is visible. It remains colourless after the sulphur has crystallized, appearing nearly white to the eye. Selenium also darkens rapidly by heat and then transmits a greyish light, which is probably due to its breaking up into crystals. It has, however, the property of becoming more transparent as it cools. Thus the optical properties of these two substances are as remarkably similar as are their chemical relations.

It will be observed that the quantity $\frac{\nu-1}{d}$, though by no means the same in both selenium and sulphur, are not far apart. There is, however, another relation which exists; it is expressed by the formula, that in selenium,

$$\nu_{se}-1 = (\nu_s-1) \frac{E}{d};$$

where ν_s is limit of refraction of sulphur, E its equivalent, and d its density. That is, that the refraction-equivalent of selenium can be found by multiplying the refraction-equivalent of sulphur by the equivalent of selenium divided by the density of that element. This is worthy of remark, as it appears that the same relation within five or six units in the second place of decimals between isobutyl iodide as compared with isobutyl chloride, and orthobromotoluene compared with chlorotoluene and benzyl chloride. With regard to benzyl chloride, I may mention that calculation for the upper limit has revealed an error due to extracting the wrong logarithm of $\sin \theta_A$. The correct result given below agrees better with the rule that $\frac{\nu-1}{d}$ is constant in isomeric bodies. As in the case of two isomeric bodies, the equivalent is the same in both, it will be seen that this result is in agreement with the relation between selenium and sulphur stated above.

It is worthy of note that chlorine and bromine resemble sulphur and selenium in tint of transmitted light. The index

of refraction for the line A in bromine is $\mu_A = 1.6260$. It occurred to me that it would be possible to obtain a probable idea of the spectrum of this element by assuming an upper limit of refraction. Taking this limit as D and F, to which I subsequently added G, I found that F gave $\theta_A = 39^\circ 44'$, $\nu = 1.4988$, and the refraction-equivalent 13.1. Dr. Gladstone, calculating from A, gives as a probable value 15.3, which would necessarily be greater than that obtained from the limit. A refraction-equivalent for ν obtained from orthobromotoluine showed that for this substance the refraction-equivalent for ν was between 14 and 15. If we assume G as the limit, then bromine comes out as 13.7. I subsequently procured a specimen of bromine. In as thin a film as I could produce, the spectra of bromine and selenium were almost indistinguishable; but the tint of bromine is decidedly more orange, and its vapour transmitted rays up to F certainly, and perhaps beyond; but in the brightest sunlight, and even when mixed with air, there was no indication of violet rays. So far as these very imperfect observations extend, they seem to support the conclusions previously arrived at by calculation. Without venturing, then, to speak at all decisively, the subject seems a promising one and likely to repay further investigation.

In the absence of data as to the spectrum of liquid chlorine, it is useless to make calculations as to any relations which might be found to subsist between it and bromine. It is, however, of importance to observe that its yellow tint is so similar to that of sulphur, that it is not improbable that the same portions of the spectrum would be affected in both. If this on further examination should turn out to be the fact, it would be one step more towards the attainment of the form of the function $\mu = \phi(\lambda)$, which would probably reveal relations of great interest toward determining the chemical constitution of bodies.

In the case of the critical angle the imaginary sine corresponds with the change from refraction to total reflexion. And this, again, to alteration of phase in the wave of the polarized ray. Is there anything similar in the limit of refraction? I think there is. If a mirror be constructed by melting selenium on a glass slide and then pressing on it a somewhat cooler glass, we shall obtain a reflecting surface on remo-

ving the glass, and also another on the corresponding surface attached to the glass. At angles near perpendicular incidence the reflected light has a certain greenish tint. This is more apparent on the side next the glass than on the free reflecting surface, but is very evident in both. It is no doubt to be expected that light not transmitted should in certain cases be reflected. If it be absorbed there must be an expenditure of energy within the medium, which we have every reason to believe acts on the wave-length within the medium and the velocity of its transmission. The importance of selenium is that it is a manageable substance, in which the critical point of transmission lies near the middle of the luminous spectrum. Bromine would no doubt prove equally interesting, but is by no means a pleasant substance to handle.

I should hardly have ventured to come before the Society with these very rough experiments, had I not hoped that some who possessed the instrumental means would be induced to make the observations. For my own part I am more than content with the humble though somewhat laborious office of computer between mathematical investigator and observer.

TABLE I.—Comparison of Sulphur and Selenium.

Selenium.						
Density. d .	Lower index. μ_A .	Upper index. μ_D .	Arc. θ_A .	Lower limit. ν	$\frac{\nu-1}{d}$.	Shortest wave- length. λ_k .
4.3	2.653	2.980	44° 9' 0"	2.3976	32502	5295.7
Sulphur.						
* d .	μ_A .	μ_D .	θ_A .	ν .	$\frac{\nu-1}{d}$	
d' 2.07 d'' 1.98	} 1.9024	1.9527	20° 32' 0"	1.8610	{ 41648 43535	

* d' is the density of native sulphur.
 d'' " " " of that from fusion.

Thus we have the following empirical relation. If E be

the equivalent of sulphur, and ν its limit of refraction,

$$\frac{\nu-1}{d'} E = 13326,$$

$$\frac{\nu-1}{d''} = 13932.$$

Again, we have

Orthobromotoluine, $\nu-1 = 5299,$

Ref. equiv. Benzyl chloride $\frac{\nu-1}{d} E = 5941.7,$

do. do. Chlorotoluine, $\frac{\nu-1}{d} E = 5907.2,$

and

Isobutyl iodide, $\nu-1 = 4749,$

Ref. equiv. Isobutyl chloride, $\frac{\nu-1}{d} E = 4163.9.$

TABLE II.—Bromine.

Spec. grav.	μ_{Δ} .	Assumed upper limit.		
		μ_D .	μ_F .	μ_G .
3.085	1.6260	give 10.9	13.1	13.7
		corresponding refraction-equivalents.		

Note on these Tables.—They can only be accepted as approximate, but the calculations have been carried quite as far as the uncertainty of the original data warrant. Under these circumstances the coincidences noticed between sulphur and selenium are of no great value, except perhaps as pointing out a likely direction in which the search for these empirical relations amongst the refractive indices should be pursued.