ART. VII.—*Miscellaneous Optical Notices*; by WOLCOTT GIBBS, M.D., Rumford Professor in Harvard University.

§ 1.

On the measurement of wave lengths by means of indices of refraction.*

IN a brief notice† communicated to the British Association for the Advancement of Science at its meeting in 1849, Prof. Stokes has given a method for measuring wave lengths, which depends upon the fact that, in substances of medium refractive power, the increment of the index of refraction in passing from one point of the spectrum to another is nearly proportional to the increment of the square of the reciprocal of the wave length. The author showed that even when the intervals were taken much longer than necessary, the error in the wave length was usually only in the eighth place of decimals. At the date of the publication of this notice the subject of wave lengths possessed but little interest. The recent development of the spectral analysis of light has given a new impulse to this branch of optics, and has rendered necessary the construction of a normal map of the entire solar spectrum. This has been most successfully accomplished by Angström,‡ but an attentive study of his work, as well as of the elaborate researches of Van der Willigen§ and Ditscheiner,|| will show that new measurements will be far from superfluous. The imperfections even of the best ruled glasses are so great that it may be reasonably doubted whether the wave lengths of very fine lines can be satisfactorily measured directly. Methods of determining such wave lengths, depending upon the comparison of the refraction and diffraction spectra, have been given by myself¶ and by Thalen.** As it seems at least desirable to multiply such methods, I will here give first a discussion of the method of Stokes in its original form, and afterward a simplification of that method which will also have its uses.

If Cauchy's formula for dispersion, $n = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}$,

* Read before the National Academy of Sciences, April 12th, 1870.

† Report of the British Association for the Advancement of Science for 1849. Notices and abstracts, p. 10.

‡ Recherches sur le Spectre Solaire. Berlin, 1869.

§ Archives du Musée Teyler, vol. i, p. 1.

|| Sitzungsberichte der k. k. Akad. der Wissenschaften Bd. I, 1864.

¶ This Journal, xlvii, March, 1869.

** Mémoire sur la détermination des longueurs d'onde des raies métalliques, 1868.

be reduced to its two first terms, and if we then eliminate the constants a and b from three equations of the form

$$n = a + \frac{b}{\lambda^2}$$

we shall obtain the three following equations, involving only wave lengths and indices of refraction:

$$\lambda_1^2 = \frac{(n_3 - n_2)}{(n_3 - n_1)\frac{1}{\lambda_2^2} + (n_2 - n_1)\frac{1}{\lambda_3^2}} \quad (1)$$

$$\lambda_2^2 = \frac{(n_3 - n_1)}{(n_2 - n_1)\frac{1}{\lambda_3^2} + (n_3 - n_2)\frac{1}{\lambda_1^2}} \quad (2)$$

$$\lambda_3^2 = \frac{(n_2 - n_1)}{(n_3 - n_1)\frac{1}{\lambda_2^2} + (n_3 - n_2)\frac{1}{\lambda_1^2}} \quad (3)$$

Of these equations (1) and (3) serve for extrapolation and (2) for interpolation. To test the degree of accuracy attainable in determining wave lengths by these formulas, I have selected the measurements made by Van der Willigen.* The indices of refraction determined by the Dutch physicist are in fact the only indices which are at once sufficiently exact and sufficiently numerous. In addition they have the great advantage of having been made with reference to lines in the solar spectrum the wave lengths of which had been measured by the same observer. There can therefore be no question of identity. As a first example of the method, I give a determination of the wave length of C, taking B as one of the lines exterior to C, and taking in succession 7 other exterior lines more refrangible than C, to combine with B. Formula (2) was therefore employed, and with the following data and results:—

B	1.61079	687.48		
C	1.61252	656.56		
D	1.61436	628.11	656.70	+0.14
11	1.61537	613.96	656.71	+0.15
13	1.61560	610.52	656.56	0.00
14	1.61728	589.56	656.71	+0.15
16	1.61978	561.80	656.76	+0.20
17	1.62064	553.19	656.79	+0.23
19	1.62143	545.83	656.87	+0.31
Mean of the errors				+0.17

In this table the first column gives the designation or number of the lines, the second its index of refraction, as determined by a Steinheil prism of 60°, the third the corresponding

* Archives du Musée Teyler, vol. i, p. 70.

wave length, according to Van der Willigen, and the fourth the wave length as found by formula (2) by combining B with each line after C in succession.

The mean of the seven values of the wave length of C thus found is 656·70, which is in excess of Van der Willigen's own determination of the value of C by 0·14. From this it appears that the method may be applied with a tolerable degree of approximation, even in the case of a flint glass prism of high dispersive power, and for indices of refraction which refer to lines at considerable angular distances from each other. The increase in the computed values of C, as the intervals between B and the second line of comparison are increased, will however clearly appear from the table. The following results were obtained with the indices of a second Steinheil prism, No. 2, of 46° 52' 25''·8, also of flint glass.

B	1·60521	B and 8a	656·21	—0·35
C	1·60694	B and 11	656·33	—0·23
8a	1·60872	B and 13	656·31	—0·25
11	1·60973	B and 16	656·38	—0·18
13	1·60998	B and 17	656·47	—0·09
16	1·61408			
17	1·61495			

The mean of which is 656·28, the error being —0·28. To determine to what extent the method applies, when flint glass prisms are used, and the indices are selected from the more refrangible portion of the spectrum, the following data were assumed:—

F	1·62917	486·39	F and G	438·88	+0·30
35	1·63244	467·00	F and 39	438·76	+0·18
37	1·63828	438·58	F and 38	438·82	+0·24
38	1·63931	434·28	G and 35	438·76	+0·18
39	1·63965	432·74	35 and 38	438·75	+0·17
G	1·64006	431·12	35 and 39	438·67	+0·09

In this table, line 37 is taken as the middle line in applying formula (2), and the results obtained by combining the other lines in pairs are given in columns 4, 5 and 6. It will be seen that, as in the case of the less refrangible portion of the spectrum, the results obtained are with this prism always too high. For the purpose of comparison, I have computed the same wave length from the indices of refraction of the second prism. The data and results are as follows:—

F	1·62332	486·39	F and G	439·07	+0·49
35	1·62657	467·00	F and 39	438·89	+0·31
37	1·63221	438·58	F and 38	438·92	+0·34
38	1·63324	434·28	G and 35	439·00	+0·42
39	1·63358	432·74	35 and 38	438·89	+0·31
G	1·63400	431·12	35 and 39	438·84	+0·26

In the case of the first prism the mean of the errors is $+0.21$, while for the second the mean of the errors is $+0.35$. From this it appears that in the more refrangible portion of the spectrum the errors are considerably greater than in the less refrangible portion, even for equal differences of wave length, and further, that the advantage in precision is with the prism having the higher dispersive power. As the probable errors of the measurements of the indices of refraction are not given, it is impossible to determine to what extent the errors in the computed wave lengths are due solely to want of precision in the indices. It is also to be remarked that, while with the second prism the errors in the less refrangible portion of the spectrum are affected with the sign $-$, in the more refrangible portion they are largely positive. The close agreement in the value of the wave length of 37 , as found by Van der Willigen, with the values as found by Ditscheiner and Angström— 438.27 and 438.28 —proves that the source of error is not an erroneous determination of this quantity. It seems therefore certain that the nearly constant errors noted above are due in part to the fact that the indices of refraction are determined only to five places of decimals, and in part to the high dispersive powers of the prisms employed, which would render it necessary to employ more than two terms in Cauchy's formula to obtain a closer approximation. As the formulas for interpolation would in this way be rendered extremely complicated, it is better, in the case of any series of observations embracing a particular part of the scale, simply to determine the mean of the errors, and to apply this mean with its proper sign to the computed values of the particular wave length to be determined by the measurement of indices of refraction. If we apply such a correction in the cases of the four series of data and results given above, we find for the corrected values of the wave-lengths the following numerical results:—

(1)	(2)	(3)	(4)
656.53	656.49	438.67	438.72
656.54	656.61	438.55	438.54
656.38	656.59	438.61	438.57
656.54	656.66	438.55	438.65
656.59	656.75	438.54	438.54
656.62		438.44	438.49

The true values being respectively 656.56 and 438.56 . These results are, I think, sufficient to show that a valuable control for the accuracy of measurements of wave lengths may be obtained even when prisms of high dispersive power are employed, provided that the intervals taken are not too large. It seems at least probable that a greater degree of precision is attainable in measuring indices in the case of substances of high

than in those of low dispersive power, partly because the angular deviations to be measured are larger, and partly because the spectral lines are less crowded together.

The following example will serve to illustrate the advantage of taking shorter intervals:—

Lines.	λ	Indices.	λ	Indices.	λ
25 <i>b</i>	518·63	1·62459	-----	1·61882	-----
26	517·51	1·62472	517·61	1·61895	517·56
27 <i>β</i>	517·07	1·62479	-----	1·61901	-----

The data are here also taken from Van der Willigen's measures with the same prisms.

When the angular distances between three spectral lines are not too great, the angular deviation of the lines may, as I find, be substituted for the indices of refraction in formulas (1), (2) and (3). The differences between the angular deviations are of course to be converted into seconds. The following results will show the degree of accuracy attainable by this method, the data being taken from Ditscheiner's* measurements of the indices of a flint prism by Steinheil of refracting angle $60^{\circ} 4' 59''$.

Kirchhoff's scale.	λ	Angular deviations.	λ	Indices.	λ	
B	593	687·06	47° 40' 55"	-----	1·61358	-----
C	694	655·95	47° 51' 19"	655·97	1·61537	655·82
--	877	613·57	48° 8' 8"	-----	1·61824	-----

From this it appears that the error in the determination of the wave-length of the middle line C is only +0·02 when the angular deviations are employed, but amounts to -0·13 when the indices of refraction are taken as the elements of the calculation. Yet the interval between B and 877 is very large.

The following data are taken from another part of the scale, the measurements being made with the same prism:—

Kirchhoff's scale.	λ	Angular deviations.	λ	Indices.	λ	
<i>b</i>	1648·8	517·13	49° 4' 16"	-----	1·62775	-----
	1655·6	516·58	49° 4' 44"	516·56	1·62782	516·61
	1693·8	514·08	49° 6' 47"	-----	1·62817	-----

Hence the error in the determination of the wave length of 1655·6 is, when the angular deviations are taken, only -0·02 and when the indices are taken +0·03. It must be borne in mind that in all the above mentioned examples the angles are those of minimum deviation. As the numbers upon Kirchhoff's scale also represent angular though not *minimum* deviations, it seemed worth while to determine how far for a short interval, these could be employed. Taking the three scale numbers of the last example, the error in the wave-length of

* Bestimmung der Wellenlängen der Fraunhoferschen Linien des Sonnenspektrums, p. 43.

1655·6 was found to be $-0\cdot38$, and when the scale numbers were taken as the sines or tangents of corresponding angles, $+0\cdot09$.

The following data are taken from the more refrangible part of the spectrum, the measurements being also those of Ditschiner, and made with the same prism:—

	2822·8	433·34	$50^{\circ} 34' 57''$	-----	1·64287	-----
G	2854·7	430·88	$50^{\circ} 37' 52''$	430·68	1·64334	430·83
	2969·7	429·90	$50^{\circ} 38' 47''$	-----	1·64352	-----

In this case the error in the wave-length of the middle line, 2854·7, is $-0\cdot20$, as determined from the angular deviations, and $-0\cdot05$, as determined from the indices. It must be borne in mind that, in this part of the spectrum, the determination both of wave lengths and of indices of refraction is difficult on account of the feeble intensity of the light.

Since only the differences between the angular deviations of the spectral lines are employed in the formulas above given, it follows that in determining wave lengths by the method in question, it is not necessary to employ a spectrometer with a divided circle and appliances for the measurement of large angles. A common spectroscope will be sufficient, if the observing telescope be provided with a filar micrometer by means of which the angular distances of any given line from two other lines of which the wave lengths are known may be measured. The researches of Angström leave nothing to be desired as regards the wave-lengths of standard lines, and the method given may prove a convenient means of determining with all requisite precision the wave lengths of metallic lines.

§ 2.

On liquids of high dispersive power.—Of the liquids which have hitherto been proposed for the construction of prisms, bisulphid of carbon unquestionably presents the greatest advantages. It is cheap, colorless, and unites a moderately high mean refractive to a very high dispersive power. By tacit consent a prism of 60° filled with this liquid has come to be adopted as a sort of standard. The disadvantages of the bisulphid are equally well known, and I have spent no little time and labor in the endeavor to find a liquid with a still higher dispersive power, less volatile, less sensitive optically to changes of temperature, and less offensive in odor. In these efforts I have not been altogether successful, no one liquid examined possessing all the qualities desired. Many organic liquids with high dispersive powers are difficult to prepare in a state of purity and speedily become discolored by absorption of oxygen from the air. Such are oil of cassia, the colorless oil obtainable from balsam of

Peru and others. The thallic alcohol of Lamy* is far too costly. The solution of silico-tungstate of sodium,† of meta-tungstate of sodium‡ and of soluble tungstic acid § as obtained by dialysis, all promised good results from their extraordinary densities, but all proved difficult to prepare in a state of purity and extremely easy of decomposition.

A solution of phosphorus in bisulphid of carbon has, according to Messrs. Dale and Gladstone,|| a dispersion of 0.225,¶ or nearly one and a half times as great as bisulphid of carbon alone, but becomes turbid on exposure to sunlight from the formation of amorphous phosphorus. It occurred to me, that, by dissolving sulphur with the phosphorus, the formation of amorphous phosphorus might be prevented, and experiment proved that this was the case. The solution, as thus obtained, has a pale yellow color, but is perfectly clear and undergoes no change by the action of light even when long continued. I have been in the habit of preparing it by dissolving one part of dry flowers of sulphur and two parts of phosphorus, in four or five parts of bisulphid of carbon, and filtering the liquid through a well dried ribbed paper filter, which is easily done. The refractive and dispersive power of the solution will of course vary with the quantity of phosphorus and sulphur dissolved. By a gentle heat the whole, or nearly the whole, of the bisulphid of carbon may be driven off, a liquid compound of sulphur and phosphorus remaining which has so high a mean refractive power that it cannot be employed with prisms having a refractive angle of more than 45° – 50° . The same end may, however, also be attained by continually adding phosphorus to a saturated solution of sulphur in bisulphid of carbon, in which phosphorus appears to be soluble without limit.

With a strong and probably saturated solution of sulphur in CS_2 , the angle between Li and D was $0^{\circ} 50' 10''$. When phosphorus was added the angle was $2^{\circ} 25' 30''$, the refracting angle of the prism being 60° . In this last case the angle between Na_1 and Na_2 was $0^{\circ} 2' 20''$. The spectrum was perfectly clear, the definition of the dark lines leaving nothing to be desired. In consequence, however, of the yellow color of the liquid there is always a marked absorption of the violet end of the spectrum.

In working with the above described solution I have employed hollow glass prisms with refracting plates cemented on with a mixture of glue and molasses. These were found to

* *Ann. de Chimie et de Physique*, 4th series, vol. iii, p. 373.

† *Ann. de Chimie et de Physique*, 4th series, vol. iii, p. 5.

‡ Scheibler in *Journal für prakt. Chemie*, lxxxiii, p. 273.

§ Graham in *Journal of the Chemical Society*, vol. ii, p. 318

|| L. and E. *Phil. Mag.*, vol. xviii, p. 30.

¶ The number 0.225 is the difference between the indices for the extreme red and violet rays.

be perfectly tight and to last for months without change. The great disadvantage in the use of a solution of sulphur and phosphorus consists in the danger of breaking the prisms; the liquid taking fire spontaneously when it has been a few seconds in contact with any porous material like wood or paper. On the other hand, however, the large quantity of sulphur present prevents the fire from spreading, a drop placed upon a piece of wood leaving after combustion only a charred spot. When not in use the prisms should be kept in an iron pot with a tight cover. In this manner I have employed and preserved two during a long and hot summer. The viscid, or rather oily, nature of the solution serves to prevent, to a great extent, the formation of ascending and descending currents from slight changes of temperature, and when the prisms are well shaken before use the definition remains perfect for a long time. In my spectroscope the prisms rest upon a plate of glass instead of upon one of metal.

§ 3.

On an advantageous form of apparatus for the study of the absorption of light in colored liquids.

In his examination of the spectra of colored fluids, Mr. Gladstone employed a hollow wedge of glass, the two refracting surfaces of which made with each other an acute angle. The wedge was filled with the liquid to be studied and so placed that the refracting edge of the analyzing prism was at right angles to the line of intersection of the two faces of the wedge. In this manner a beam of light was obtained which represented different thicknesses of the absorbing liquid, and the resulting spectrum became a complete absorption diagram. In using this apparatus I found the angular deviation produced by the wedge a source of considerable inconvenience. In addition it is easy to see that the wedge itself produces a certain amount of chromatic dispersion. To remedy these defects and at the same time retain the advantages of the method, I have devised what may be termed a double wedge. Two hollow wedges, of glass or metal, are placed together in such a manner that the first and last surfaces of the bounding plates of glass are parallel. The two wedges are separated by a single plate of glass with parallel surfaces. The base of each wedge, or acute-angled prism, is bored for the insertion of a cork or stopper. The construction of the apparatus will be readily understood from the diagram. In using it with a colored aqueous solution one of the hollow prisms, or wedges, is to be filled with distilled water, the other with the aqueous solution to be examined. The incident beam of sunlight is then allowed to fall perpendicularly upon

either surface, and the slit of the spectroscope is placed so as to be perpendicular to the two lines of intersection of the three refracting plates of the double wedge. In this manner a complete absorption diagram is obtained by the various thicknesses of the liquid examined. For substances soluble in alcohol, ether, &c., one of the hollow wedges must be filled with the colorless solvent, whatever be its nature. By this means all angular deviation and prismatic dispersion are avoided, as the coloring matter does not sensibly change the refractive power of the liquid in which it is dissolved, and the incident beam passes through without change in direction. In my apparatus the wedges have acute angles of about 15° . This I find to be quite sufficient for most purposes, as it is easy to increase or diminish the quantity of substance dissolved. When it is wished to examine the absorption produced by a definite thickness of liquid or by different thicknesses in succession, the double wedge is to be so placed that the slit of the spectroscope shall be parallel to the lines of intersection of the faces of the wedges. By moving the wedge to one side or the other all thicknesses of liquid, from 0 to the maximum, obtainable with the apparatus used, may be successively examined.

§ 4.

On tests for the perfection and parallelism of plane surfaces of glass.

When a plano-convex lens of long radius of curvature is placed upon a plane surface of glass and the system is illuminated by an obliquely incident beam of monochromatic light as, for example, by a sodium flame, the well known phenomenon of Newton's rings is observed with remarkable distinctness and perfection of definition. The symmetry of the rings will depend, in part, on the perfection of figure of the lens, in part on that of the plane surface. An extremely minute deviation from a perfect plane will produce a marked distortion of the circular figure of the ring nearest the center. That this distortion is, or is not due to the lens may be determined by rotating the lens round its optical axis normal to the plane. No change of figure will be seen if the lens is perfect in form and the inequality is in the plane surface only. Different parts of the plane surface may of course be tested in succession, by moving the lens from point to point, and if necessary the rings may be observed with a telescope.

Prof. Rood, of New York, has suggested for the observation of Newton's rings a method which permits of the employment of a lens of comparatively small radius of curvature and a microscope. In his arrangement the lens and plate of glass are placed upon the stage of the microscope, the light from beneath being cut off, and monochromatic light is then thrown down

upon the system by means of a plate of glass with parallel surfaces inclined to the axis of the microscope at a convenient angle and placed between the objective and the plano-convex lens. In this manner the rings are seen with great distinctness and beauty, and the arrangement is particularly compact and convenient.

The interference bands of Talbot afford a method not merely of observing with great precision the inequalities of surface and want of parallelism of the faces of plates of glass, but also of photographing these defects and obtaining a permanent chart of the glass which may be of material assistance in correcting its figure. It is only necessary for this purpose to place the glass to be examined near to the object glass of the collimator and perpendicular to its axis, so as to intercept that half of the bundle of parallel rays which falls upon the first surface of the first prism nearest its refracting edge. If the plate has perfectly plane and parallel surfaces the interference bands will be sharply defined and parallel in the whole field of view. The slightest inequality of surface, or inclination of the faces, will produce curvature or distortion of the bands, and, if the eyepiece of the observing telescope be removed, the image may be received on a sensitive plate and photographed. The number of prisms to be employed in a particular case will depend upon the thickness of the plate of glass examined and, in general terms, upon its dispersive power. For a piece of French plate glass four millimeters in thickness, two bisulphid of carbon prisms of 60° must be used to produce a sufficient separation of the interference bands to enable them to be seen distinctly. More prisms must be used for thicker plates and in this way a limit is soon reached at which the method ceases to be applicable.

Cambridge, May 1st, 1870.