

XXX. *On the Change of Refrangibility of Light.* By G. G. STOKES, M.A., F.R.S.,  
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1. THE following researches originated in a consideration of the very remarkable phenomenon discovered by SIR JOHN HERSCHEL in a solution of sulphate of quinine, and described by him in two papers printed in the Philosophical Transactions for 1845, entitled ‘On a Case of Superficial Colour presented by a Homogeneous Liquid internally colourless,’ and ‘On the Epipolic Dispersion of Light.’ The solution of quinine, though it appears to be perfectly transparent and colourless, like water, when viewed by transmitted light, exhibits nevertheless in certain aspects, and under certain incidences of the light, a beautiful celestial blue colour. It appears from the experiments of Sir JOHN HERSCHEL that the blue colour comes only from a stratum of fluid of small but finite thickness adjacent to the surface by which the light enters. After passing through this stratum, the incident light, though not sensibly enfeebled nor coloured, has lost the power of producing the same effect, and therefore may be considered as in some way or other qualitatively different from the original light. The dispersion which takes place near the surface of this liquid is called by Sir JOHN HERSCHEL *epipolic*, and he applies the term *epipolized* to a beam of light which, having been transmitted through a quiniiferous solution, has been thereby rendered incapable of further undergoing epipolic dispersion. In one experiment, in which sun-light was used, a feeble blue gleam was observed to extend to nearly half an inch from the surface. As regards the dispersed light itself, when analysed by a prism it was found to consist of rays extending over a great range of refrangibility: the less refrangible extremity of the spectrum was however wanting. On being analysed by a tourmaline, it showed no signs of polarization. A special experiment showed that the dispersed light was perhaps incapable, at any rate not peculiarly susceptible, of being again dispersed.

2. In a paper ‘On the Decomposition and Dispersion of Light within Solid and Fluid Bodies,’ read before the Royal Society of Edinburgh in 1846, and printed in the 16th volume of their Transactions, as well as in the Philosophical Magazine for June 1848, Sir DAVID BREWSTER notices these results of Sir JOHN HERSCHEL’s, and states the conclusions, in some respects different, at which he had arrived by operating in a different way. The phenomenon of internal dispersion had been discovered by him some years before, and is briefly noticed in a paper read before the Royal Society

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of Edinburgh in 1833\*. It is described at length, as exhibited in the particular case of fluor-spar, in a paper communicated to the British Association at Newcastle in 1838†. In Sir DAVID BREWSTER's experiments the sun's light was condensed by a lens, and so admitted into the solid or fluid to be examined ; which afforded peculiar facilities for the study of the phenomena. On examining in this way a solution of sulphate of quinine, it was found that light was dispersed, not merely close to the surface, but at a long distance within the fluid : and Sir DAVID BREWSTER was led to conclude that the dispersion produced by sulphate of quinine was only a particular case of the general phenomenon of internal dispersion. On analysing the blue beam by a rhomb of calcareous spar, it was found that a considerable portion of it, consisting chiefly of the less refrangible rays, was polarized in the plane of reflexion, while the more refrangible of its rays, constituting an intensely blue beam, had a different polarization.

3. On repeating some of Sir JOHN HERSCHEL's experiments, I was immediately satisfied of the reality of the phenomenon, notwithstanding its mysterious nature, that is to say, that an epipolized beam of light is in some way or other qualitatively different from the light originally incident on the fluid. On making the observation in the manner of Sir DAVID BREWSTER, it seemed no less evident that the phenomenon belonged to the class of internal dispersion‡. Nevertheless, the singular phenomenon discovered by Sir JOHN HERSCHEL manifested itself even in this mode of observation. If indeed the vessel containing the solution were so placed that the image of the sun in the focus of the lens lay a little way inside the fluid, the phenomenon was masked, because the increase of intensity due to an increase of concentration in approaching the focus made up for the decrease of intensity due to passing out of the blue band. But when the vessel was moved so that the focus of the lens fell either further inside the fluid or else outside the vessel, the narrow blue band adjacent to the surface was seen *as well as* the blue beam which shot far into the fluid. Light which has been "epipolized" by transmission through a moderate thickness of the solution is indeed capable of undergoing further dispersion, but not *epipolic* dispersion, *if that term be restricted* to the dispersion by which the narrow blue band is produced. It was no doubt of great importance to assign to the phenomenon its true place as a member of the class of phenomena of internal dispersion. Nevertheless the mystery was by no means cleared up ; rather, we were prepared to expect something of the same sort

\* Edinburgh Transactions, vol. xii. p. 542.

† Eighth Report.—Transactions of the Sections, p. 10.

‡ By this, I merely mean that, to take a particular example, the exhibition of a blue light by a solution of sulphate of quinine appeared to be a phenomenon of the same nature as the exhibition of a red light by a solution of the green colouring matter of leaves, although the latter does not manifest the same singular concentration as the former in the neighbourhood of the surface by which the light enters ; and the latter had already been observed by Sir DAVID BREWSTER, and the phenomenon designated as *internal dispersion*. I make this remark because Sir DAVID BREWSTER has applied this same term to another class of phenomena which are totally different.

in other instances of internal dispersion. In fact, the mystery consisted, not in the narrowness of the stratum from which most of the blue light came, but in the circumstance that it was possible for light, by passing across such a stratum, to be deprived of the power of producing the same effect again, without, apparently, being altered in any other respect.

4. To one who regards light as a subtle and mysterious agent, of which the laws indeed are in a good measure known to us, but respecting the nature of which we are utterly ignorant, the phenomenon might seem merely to make another striking addition to the modes of decomposition with which we were already acquainted. But in the mind of one who regards the theory of undulations as being for light what the theory of universal gravitation is for the motions of the heavenly bodies, it was calculated to excite a much more lively interest. Whatever difficulty there might be in explaining how the effect was produced, we ought at least to be able to say what the effect was that had been produced; wherein, for example, epipolized light differed from light which had not undergone that modification.

In speculating on the nature of the phenomenon, there is one point which deserves especial attention. Although the passage through a thickness of fluid amounting to a small fraction of an inch is sufficient to purge the incident light from those rays which are capable of producing epipolic dispersion, the dispersed rays themselves traverse many inches of the fluid with perfect freedom. It appears therefore that the rays producing dispersion are in some way or other of a different nature from the dispersed rays produced. Now, according to the undulatory theory, the nature of light is defined by two things, its period of vibration, and its state of polarization. To the former corresponds its refrangibility, and, so far as the eye is a judge of colour, its colour\*. To a change, then, either in the refrangibility or in the state of polarization we are to look for an explanation of the phenomenon.

5. Regarding it at first as an axiom that the dispersed light of any given refrangibility could only have arisen from light of the same refrangibility contained in the incident beam, I was led to look in the direction of polarization for the required change in the nature of the light. Since a fluid has no axes, circular polarization is

\* It has been maintained by some philosophers of the first eminence that light of definite refrangibility may still be compound, and though no longer decomposable by prismatic refraction might still be so by other means. I am not now speaking of compositions and resolutions depending upon polarization. It has even been suggested by the advocates of the undulatory theory, that possibly a difference of properties in lights of the same refrangibility might correspond to a difference in the law of vibration, and that lights of given refrangibility may differ in tint, just as musical notes of given pitch differ in quality. Were it not for the strong conviction I felt that light of definite refrangibility is in the strict sense of the word homogeneous, I should probably have been led to look in this direction for an explanation of the remarkable phenomena presented by a solution of sulphate of quinine. It would lead me too far from the subject of the present paper to explain the grounds of this conviction. I will only observe that I have not overlooked the remarkable effect of absorbing media in causing apparent changes of colour in a pure spectrum; but this I believe to be a subjective phenomenon, depending upon contrast.

the only kind which can here come into play. As some fluids are doubly refracting, transmitting right-handed and left-handed circularly polarized light with different velocities, so, it might be, this fluid was doubly absorbing, absorbing say right-handed circularly polarized light of certain refrangibilities with great energy, and freely transmitting left-handed. The right-handed light, absorbed, in the sense of withdrawn from the incident beam, might have been more strictly speaking scattered, and thereby depolarized. The common light so produced would be equivalent to two streams, of equal intensity, one of right-handed, and the other of left-handed circularly polarized light. Of these the latter would be freely transmitted, while the former would be scattered anew, and so on. Yet this hypothesis, sufficiently improbable already, was not enough. New suppositions were still required, to account for the circumstance that an epipolarized beam, when subjected to prismatic analysis with a low magnifying power, exhibited no bands of absorption in the region to which, as regards their refrangibility, the dispersed rays principally belong; so that altogether this theory bore not the slightest semblance of truth.

6. I found myself thus fairly driven to suppose that the change of nature consisted in a change of refrangibility. From the time of NEWTON it had been believed that light retains its refrangibility through all the modifications which it may undergo. Nevertheless it seemed to me less improbable that the refrangibility should have changed, than that the undulatory theory should have been found at fault. And when I reflected on the extreme simplicity of the whole explanation if only this one supposition be admitted, I could not help feeling a strong expectation that it would turn out to be true. In fact, we have only to suppose that the invisible rays beyond the extreme violet give rise by internal dispersion to others which fall within the limits of refrangibility between which the retina of the human eye is affected, and the explanation is obvious. The narrowness of the blue band observed by Sir JOHN HERSCHEL would merely indicate that the fluid, though highly transparent with regard to the visible rays, was nearly opaque with regard to the invisible. According to the law of continuity, the passage from almost perfect transparency to a high degree of opacity would not take place abruptly; and thus rays of intermediate refrangibilities might produce the blue gleam noticed by Sir JOHN HERSCHEL, or the blue cylinder, or rather cone, observed by Sir DAVID BREWSTER. We should thus, too, have an immediate explanation of a remarkable circumstance connected with the blue band, namely that it can hardly be seen by strong candle-light, though readily seen by even weak daylight. For candle-light, as is well known, is deficient in the chemical rays situated beyond the extreme violet.

7. My first experiments were made with coloured glasses. A test tube was about half filled with a solution consisting of disulphate of quinine dissolved in 200 times its weight of water acidulated with sulphuric acid. The tube, having been first covered with black paper, with the exception of a hole by which the light might enter, was placed in a vertical position in front of a window, the hole being turned



towards the light. On looking down from above, in a direction nearly parallel to the surface of the glass, a blue arc was well seen, extending only a very short distance into the fluid, and situated immediately behind the hole. As this arc, though extremely distinct, was not of course what could be called brilliant, I did not at first venture, for the experiment I had in view, to use any but pale glasses. Having no direct means of determining which were opaque with regard to the invisible rays situated beyond the extreme violet, I sought among a collection of orange, yellow, and brown glasses, which, from transmitting mainly the less refrangible rays, seemed the most likely to absorb the chemical rays. I presently found a pale smoke-coloured glass, which, when placed immediately in front of the hole, prevented the formation of the blue arc, although when placed immediately in front of the eye it transmitted a large proportion of the light of which the arc consisted. The colour of the arc was of course modified, and rendered more nearly white.

On trying other pale glasses, I found one of a puce colour, which, when placed in front of the hole, allowed the arc to be formed, though it absorbed it when placed in front of the eye. A yellow, and likewise a yellowish green glass allowed the arc to be seen in both positions; but its colour was decidedly different according as the glass was placed in front of the hole or in front of the eye. The breadth, too, of the arc was differently affected by different coloured glasses placed in front of the hole, some causing the light to be more, and others less concentrated towards the surface of the test tube than when the incident light was unimpeded.

8. The sun's light was next reflected horizontally into a darkened room, and allowed to pass through a hole in a vertical board which was placed in the window. The hole contained a lens of rather short focus. On placing a test tube containing the solution, in a vertical position, in front of the lens, at such a distance that the focus lay some way inside the fluid, the narrow blue band described by Sir JOHN HERSCHEL and the blue beam mentioned by Sir DAVID BREWSTER were seen independently of each other. On trying different coloured glasses, which were placed, first in front of the fluid, and then in front of the eye, it was found that the blue beam, as had previously proved to be the case with the narrow band, was for the most part differently affected according as the glass was placed so as to intercept the incident or the dispersed light. Moreover, the long blue beam and the narrow band did not behave in the same manner under the action of the same coloured glass.

9. To my own mind these experiments were conclusive as to the fact of a change of refrangibility. Admitting that the effect of a coloured glass is simply to stop a certain fraction of the incident light, that fraction being a function of the refrangibility, it is plain that the results can be explained in no other way. It must be confessed however that these results are merely an extension of that which precisely constitutes the peculiarity of the phenomenon. For, take the case of the narrow blue band formed by ordinary daylight. Imagine a glass vessel with parallel sides to be filled with a portion of the solution, and placed so as to intercept, first the incident,

and then the dispersed light. In the first position the light incident on the fluid under examination would be "epipolized" by transmission through the fluid contained in the vessel, and therefore the blue band would be cut off, whereas when the vessel was held in front of the eye the blue band would be freely transmitted. Hence the effects of the coloured glasses are analogous to, but less striking than, the effect of a stratum of the solution of sulphate of quinine in the imaginary experiment above described. There is to be sure one important difference in the two cases, namely, that in the case of the stratum of fluid the epipolic dispersion which is prevented in the fluid under examination is produced near the first surface of the stratum, whereas no such dispersion is produced, or at any rate necessarily produced, in the coloured glasses. Whatever the reader may think of the results obtained with coloured glasses, the next experiment it is presumed will be deemed conclusive.

10. The board in the window containing the lens having been replaced by a pair of boards adapted to form a vertical slit, the sun's light was reflected horizontally through the slit, and transmitted through three Munich prisms placed one after the other close to it. A tolerably pure spectrum was thus formed at the distance of some feet from the slit. A test tube containing the solution was then placed vertically a little beyond the extreme red of the spectrum, and afterwards gradually moved horizontally through the colours. Throughout nearly the whole of the visible spectrum the light passed through the fluid as it would have done through so much water; but on arriving nearly at the violet extremity a ghost-like gleam of pale blue light shot right across the tube. On continuing to move the tube, the blue light at first increased in intensity and afterwards gradually died away. It did not however cease to appear until the tube had been moved far beyond the violet extremity of the spectrum visible on a screen. Before disappearing, the blue light was observed to be confined to an excessively thin stratum of fluid adjacent to the surface by which the light entered, whereas when it first appeared, namely when the tube was placed a little short of the extreme violet, the blue light had extended completely across it. It was certainly a curious sight to see the tube instantaneously lighted up when plunged into the invisible rays: it was literally *darkness visible*. Altogether the phenomenon had something of an unearthly appearance.

11. Since the fluid is so intensely opaque with regard to rays of extreme refrangibility, it might be expected, that, though it appears transparent and colourless when examined merely by viewing a white object through it, it would yet exhibit a very sensible absorbing action with regard to the extreme violet rays when subjected to prismatic analysis. To try whether such were really the case, I reflected the sun's light horizontally through a slit, at which was placed a test tube filled with the liquid, and analysed the line of light by a prism, the eye being defended by a deep blue glass. I was barely able to make out the fixed line H in Plate XXV., that is, the less refrangible band of the pair, although in similar circumstances I can generally see about as far beyond the more refrangible band as it is beyond H. However, to make the result

more decisive by using a greater thickness, as well as to render the observation strictly differential, I placed a tumbler filled with water behind the slit, the blue glass before it, and then viewed the slit through the prism. I saw as far as usual into the violet. The water was then poured out and replaced by the solution of sulphate of quinine, which, when viewed by transmitted light, appeared as transparent as the water which it had replaced. When the tumbler was now placed behind the slit, the blue beam of dispersed light was observed to extend quite across it, a distance of about three inches, and would evidently have gone much further. On viewing the slit through the prism, the spectrum was found to be cut off about half-way between the fixed lines G and H. The termination was pretty definite, which indicates that, at least for that part of the spectrum, the absorbing energy of the fluid rapidly increased with the refrangibility of the light; there was, however, an evident diminution of intensity produced by the fluid, extending from the termination of the spectrum to near G.

12. There could no longer be any doubt, either as to the fact of a change of refrangibility, or as to the explanation thereby of the remarkable phenomenon exhibited by sulphate of quinine. Epipolized light is merely light which has been purged of the invisible, or at most feebly illuminating rays more refrangible than the violet; and the term itself, which in fact was only adopted provisionally by Sir JOHN HERSCHEL, and which has now served its purpose, may henceforth be discarded, especially as it is calculated to convey a false impression respecting the cause of the phenomenon. It remained to examine other instances of internal dispersion, of which, according to Sir DAVID BREWSTER's observations, the dispersion produced by sulphate of quinine is only a particular case; to endeavour to make out the laws according to which a change of refrangibility takes place; and, if possible, to account for these laws on mechanical principles.

13. In giving an account of my further experiments, I think it best to describe in detail the phenomena observed in some of the more remarkable instances of internal dispersion before attempting to draw any general conclusions. It will save repetition to explain in the first instance the methods of observation employed, which on the whole may very fairly be divided into four, though occasionally it was convenient to employ intermediate methods, or a combination of two of them. Of course I frequently availed myself of Sir DAVID BREWSTER's method of observation, in which the effect of the incident light is studied as a whole; but the methods here referred to relate to an investigation of the separate offices of the portions of light of different degrees of refrangibility which are found in the incident beam. As my researches proceeded, new methods of observation suggested themselves, but these will be described in their place.

#### *Methods of Observation employed.*

FIRST METHOD.—The sun's light was reflected horizontally through a small lens, which was fixed in a hole in a vertical board. The cone of emergent rays was

allowed to enter the solid or fluid examined. A coloured glass or other absorbing medium was then placed, first so as to intercept the incident rays, and then between the substance examined and the eye. For shortness' sake these positions will be designated as *the first* and *the second*. Sometimes a coloured glass was allowed to remain in front of the hole, and a second glass was added, first in front of the hole and then in front of the eye.

SECOND METHOD.—The sun's light, reflected as before, was transmitted through a series of three or four Munich prisms placed one immediately after the other, and each nearly in the position of minimum deviation. It was then transmitted through a small lens in a board close to the last prism, and so allowed to enter the body to be examined, which was generally placed so that the first surface coincided, or nearly so, with the focus of the lens. The diameter of the lens was much smaller than the breadth or height of the prisms, so that the lens was completely filled with white light, the component parts of which however entered in different directions. Regarding the image of the sun in the focus of the small lens as a point, we may conceive the light incident on the body under examination as consisting of a series of cones, corresponding to different refrangibilities, the axes of which lay in a horizontal plane and intersected in the centre of the lens, the vertices being arranged in a horizontal line near the surface of the body examined.

THIRD METHOD.—The sun's light was reflected horizontally through a vertical slit, and received on the prisms, which were arranged as before, but placed at the distance of several feet from the slit. A large lens of rather long focus was placed immediately after the last prism, with its plane perpendicular, or nearly so, to the beam of light which had passed through the prisms, and with its centre about the middle of this beam. The body examined was placed at the distance of the image of the slit, or nearly so.

FOURTH METHOD.—Everything being arranged as in the third method, a board with a small lens of short focus was placed at the distance of the image of the slit, or between that and the image of the sun, which was a little nearer to the prisms, inasmuch as the focal length of the large lens commonly employed, though much smaller, was not incomparably smaller than the distance of the lens from the slit. A second slit was generally added immediately in front of the small lens. The body examined was placed at the focus of the small lens. The dispersed light was viewed from above, and analysed by a prism, being refracted sideways.

The object of these several arrangements will appear in the course of the paper. The prisms employed consisted, three of them of flint glass and one of crown. The refracting angles of the former were about  $43^\circ$ ,  $33^\circ$ , and  $24^\circ$ , and that of the latter about  $45^\circ$ . The refracting faces of the smallest of the prisms (the flint of  $43^\circ$ ) were 1.35 inch high and 1.60 long. The small lens used was one or other of a pair of which the apertures were 0.34 inch and 0.22 inch, and the focal lengths 0.75 inch and 0.50 inch. The focal length of the large lens generally used was about twelve inches.

Once or twice a lens was tried which had a focal length about three times as great, but the light proved too faint for most purposes. In the third method it was sometimes convenient to employ a lens of only  $6\frac{1}{2}$  inches focal length, but the 12-inch lens was employed in the fourth method, except on a few occasions, when the lens of 36 inches focal length was used. With the 12-inch lens the length of the spectrum from the fixed line B to H was usually about an inch and a quarter.

It will be convenient for the purposes of this paper to employ certain terms in a particular sense, but as some of these terms relate to phenomena which have not yet been described, it will be well previously to relate in detail what was observed in one remarkable instance of internal dispersion.

*Solution of Sulphate of Quinine.*

14. The effects of some pale coloured glasses in the case of this fluid have already been mentioned. But there is one glass of which the effect is still more striking. It is well known that a deep cobalt blue glass is highly transparent with regard to the chemical rays. Accordingly I found that a blue glass, so deep that only the brighter objects in a room could be seen through it, produced but very little effect when placed so as to intercept the light incident on the fluid. When placed immediately in front of the eye, at first everything disappeared except the light reflected from the convexities of the glass tube; but when the eye became a little accustomed to the darkness it was possible to make out the existence of the band. The contrast between the effects of this glass and of the pale brown glass already mentioned was most striking.

15. When the fluid was examined by the second method, the dispersed light was found to consist of two beams, separated from each other at their entrance into the fluid, that is, at the vertical surface of separation of the fluid and the containing vessel, and afterwards still further separated by divergence. Of course each beam must have been made up of a series of cones having their axes diverging from the centre of the lens, and their vertices situated at its focus. The first beam, or that which was produced by light of less refrangibility, consisted of the brighter colours of the spectrum in their natural order. It had a discontinuous, sparkling appearance, and was plainly due merely to motes which were suspended in the fluid. On being viewed from above through a NICOL'S prism, it was found to consist chiefly of light polarized in the plane of reflexion. Taken as a whole, it served as a fiducial line to which to refer the position of the second beam, and thereby judge of the refrangibility of the rays by which it was produced.

This second beam was a good deal the brighter of the two. Its colour was a beautiful sky-blue, which was nearly the same throughout, but just about its first border, that is, where it arose from the least refrangible of those rays which were capable of producing it, the colour was less pure. It had a perfectly continuous appearance. When viewed from above through a doubly refracting achromatic prism of quartz,

which allowed a direct comparison of the two images, it offered no traces of polarization. It was produced by light polarized in a vertical or horizontal plane as well as by common light, and in that case, as well as in the former, manifested no traces of polarization\*.

The short distance that the more refrangible rays were able to penetrate into the fluid might readily be perceived in this experiment, but the second method of observation was not adapted to bring out this part of the phenomenon.

16. On examining the fluid by the third method, the result was very striking, although of course only what might have been anticipated. The principal fixed lines of the violet, and of the chemical parts of the spectrum beyond, were seen with beautiful distinctness as dark planes interrupting an otherwise perfectly continuous mass of blue light. To see any particular fixed line with most distinctness, it was of course necessary to hold the eye in the corresponding plane, when the dark plane was foreshortened into a dark line. From the red end of the spectrum, as far as the line G, or thereabouts, the light passed freely through the fluid, or at least was only reflected here and there from motes held in mechanical suspension. About G the dispersion just commenced to be sensible, and there were traces of that line seen as a dark plane interrupting a mass of continuous but excessively faint light. For some distance further on the dispersed light remained so faint that it might have been passed over if not specially looked for. It was about half-way between G and H, or a little before, that it first became so strong as to arrest attention, and a little further on it became very conspicuous, the tint meanwhile changing to a pale sky-blue. The light was very copious about the two broad bands of the group H, and for some distance from H towards G. Some of the fixed lines less refrangible than H were very plain, and beyond H a good number were visible, which will presently be further described. The whole system of fixed lines thus visible as interruptions in the dispersed light had a resolvable appearance; but with a very narrow slit and a lens of long focus at the prisms the light would have been too faint for convenient observation.

The dispersed light about G, and for some distance further on, was so very faint that I might have overlooked it had it not arrested my attention when observing by the fourth method; indeed, I have sometimes specially looked for it in the third arrangement without having been able to see it. Practically speaking, the dispersion might be said to commence about half-way between G and H.

\* These two results, namely, that the blue beam which constitutes the greater part of the light dispersed by a solution of sulphate of quinine is unpolarized, or according to his expression possesses a *quaquaversus* polarization, and that that still remains the case when the incident light is polarized, have been already announced by Sir DAVID BREWSTER, who appears to have been led to attend to the polarization of the light from Sir JOHN HERSCHEL's observation, that the blue light arising from epipolic dispersion in a solution of sulphate of quinine was unpolarized. It seemed important however to repeat the observation on the blue beam obtained in a state of isolation.

17. On refracting the whole system sideways through a prism of moderate angle held in front of the eye, the fixed lines became confused, and the finer ones disappeared. The edges of the broad bands H were tinged with prismatic colours, like the edges of two slips of black velvet placed on a sheet of pale blue paper, and viewed through a prism. This experiment exhibits the compound character of the dispersed light, notwithstanding the perfect homogeneity of the incident light.

18. The third method of observation is well adapted to bring into view the variation in the absorbing energy of the medium corresponding to a variation in the refrangibility of the incident rays. When the eye is placed vertically over the vessel containing the solution, so that the dark planes corresponding to the fixed lines of the spectrum are projected into dark lines, of which the length is not exaggerated by obliquity, the boundary of the dispersed light is projected into a curve, which serves to represent to the eye the relation between the absorbing power of the medium and the refrangibility of the incident light. This curve is not exactly that which Sir JOHN HERSCHEL has treated of in the theory of absorption, and considered as the type of the absorbing medium to which it is applied, but nevertheless it serves much the same purpose. It is true, that, independently of any change in the absorbing energy of the medium, an increasing faintness in the dispersed light would produce to a certain extent an approximation of the curve to its axis; but practically, in the case of sulphate of quinine, as well as in a great many others, the appearance is such as to leave no doubt as to the existence of a most intense absorbing energy on the part of the medium with respect to rays of very high refrangibilities\*.

In the case of a solution of sulphate of quinine of the strength of one part of the disulphate to 200 parts of acidulated water, it has been already stated that a portion of the rays which are capable of producing dispersed light passed across a thickness of 3 inches. On forming a pure spectrum, the fixed line H was traced about an inch into the fluid. On passing from H towards G, the distance that the incident rays penetrated into the fluid increased with great rapidity, while on passing in the contrary direction it diminished no less rapidly, so that from a point situated at no great distance beyond H to where the light ceased, the dispersion was confined to the immediate neighbourhood of the surface. When the solution was diluted so as to be only one-tenth of the former strength, a conspicuous fixed line, or rather band of sensible breadth, situated in the first group of fixed lines beyond H, was observed to penetrate about an inch into the fluid. On passing onwards from the band above-mentioned in the direction of the more refrangible rays, the distance that the incident rays penetrated into the fluid rapidly decreased, and thus the rapid increase in the absorbing energy of the fluid was brought into view in a part of the spectrum in

\* I should here remark, that, after the researches described in this paper had far advanced, I met accidentally with a passage in the *Comptes Rendus*, tom. xvii. p. 883, in which M. ED. BECQUEREL mentions a solution of acid sulphate of quinine as a medium eminently remarkable for its absorbing power with respect to the rays more refrangible than H.



which, with the stronger solution, it could not be so conveniently made out, inasmuch as the posterior surface of the space from which the dispersed light came almost confounded itself with the anterior surface of the fluid.

The high degree of opacity with regard to rays of great refrangibility which the addition of so small a proportion of sulphate of quinine is sufficient to produce in water is certainly very remarkable; nevertheless it is only what I have constantly observed while following out these researches.

19. In observing by the fourth method, the part of the spectrum to which the incident light belonged was determined sometimes by the colour, sometimes by means of the fixed lines of the spectrum. It almost always happened that there were motes enough suspended in the fluid to cause a portion of the dispersed beam to consist merely of light which had undergone ordinary reflexion. When the whole dispersed beam was analysed by a prism, the beam which consisted of light reflected from motes was separated from the rest; it was in general easily recognised by its sparkling appearance, but at any rate was known by its consisting almost wholly of light polarized in the plane of incidence, whereas the truly dispersed light was unpolarized. It consisted of course of light of definite refrangibility, the same as that of the incident light, and thus served as a fiducial line to which to refer by estimation the refrangibilities of the component parts of the dispersed light. Of course this part of the observation was possible only when the incident rays belonged to the visible part of the spectrum.

On moving the lens horizontally through the colours of the spectrum, in a direction from the red to the violet, it was found that the dispersion was first perceptible in the blue. When the dispersed light was separated by a prism from the light reflected from motes, it was found to consist of an exceedingly small quantity of red; further on some yellow began to enter into its composition; further still, perhaps about the junction of the blue and indigo, the dispersed beam began to grow brighter, and was found on analysis to contain some green in addition to the former colours. In the indigo it got still brighter, and when viewed as a whole was somewhat greenish. Further still it became something of a pale slaty blue, and was found on analysis to contain some indigo, or at least highly refrangible blue. On proceeding further the dispersed light became first of a deeper blue and then, a little short of the fixed line H, whiter. At a considerable distance beyond H the dispersed light was if anything a shade more nearly white.

By this method of observation the dispersion can be detected earlier in the spectrum than by the third method, and moreover the change in the colour of the dispersed light is much more easily perceived; indeed the most striking part of this change takes place while the dispersed light is so very faint that it can hardly be seen in observing by the third method; moreover, even in the bright part of the dispersed beam, it is not at all easy by the latter method to make out the change of tint corresponding to a change in the refrangibility of the incident rays, because the tint

changes so gradually and so slightly that the eye glides from one part of the dispersed beam to another without noticing any change.

20. It has been already mentioned that the blue beam of dispersed light seen in a solution of sulphate of quinine was produced whether the incident light was polarized in or perpendicularly to the plane of reflexion, or more properly plane of dispersion, that is, the plane containing the incident ray and that dispersed ray which enters the eye. A question naturally presents itself, whether the intensity of the dispersed light is strictly the same in the two cases. By combining a lens of rather short focus and a doubly refracting prism with the four prisms, I satisfied myself that the difference of intensity, if there were any, was not great, but the experiment presented some practical difficulties. However, the result of the following experiment appeared to be as decisive as a negative result could well be.

The arrangement being the same as in the third method, but the lens in front of the prisms having a focal length of only 6·5 inches, the incident light was polarized in a vertical plane previously to passing through the slit, by transmission through a pile of plates. The two beams of light were seen as usual in the fluid, namely, the blue beam due to internal dispersion, and the fainter coloured beam due to motes. The former of these, which was quite separate from the latter, exhibited the principal fixed lines belonging to the highly refrangible part of the spectrum. A plate of selenite was then interposed immediately in front of the vessel, so as to modify the polarization of the light entering the fluid. This plate was obtained by an irregular natural cleavage, and was cemented with Canada balsam between two discs of glass. When examined by polarized light it exhibited a succession of beautiful and varied tints, according to the various thicknesses of the different parts. Now when the plate was moved about in front of the vessel, without altering its perpendicularity to the incident light, different portions of the beam due to motes were observed to disappear and reappear, or at least to become faint and then bright again, so that a person ignorant of the cause, and not looking at the disc, might have supposed that the observer had been holding in front of the vessel a piece of dirty glass, having the dirt laid on in patches; but in whatever manner the disc was moved in its own plane without rotation, or turned round an axis perpendicular to its plane, not the slightest perceptible change was produced in any part of the blue beam.

#### *Explanation of Terms.*

21. In all the experiments described in this paper in which a spectrum was formed for the sake of examining the separate action of portions of light of different refrangibilities, the length of the spectrum was horizontal, so that the fixed lines were vertical. Nevertheless it will be convenient, for the sake of shortness, to use the prepositions *above* and *below* to signify respectively *on the more refrangible side of* and *on the less refrangible side of*.

The principal fixed lines of the visible spectrum will be denoted by letters in ac-

cordance with FRAUNHOFER's admirable map. These lines are now too well known to need description.

The only map of the fixed lines of the chemical spectrum which I had for a good while after these researches were commenced is Professor DRAPER's, which will be found in the twenty-second volume of the Philosophical Magazine (1843). Of course this map cannot be compared for accuracy of detail with FRAUNHOFER's map of the visible spectrum, nor does it profess to give more than some of the most conspicuous lines selected from among a great multitude. The suppression of so many lines, without any representation by shading of their general effect, renders it difficult to identify those which are laid down, at least if I may judge from my own observations; besides, Professor DRAPER's spectrum was so much purer than the one with which I found it most convenient to work, that the two are not comparable with each other.

22. I have made a sketch of the fixed lines from H to the end, which accompanies this paper. The fixed lines of the visible spectrum are so well known that I thought it unnecessary to begin before H. A solution of sulphate of quinine is a very good medium for showing the lines, but a yellow glass, which will be mentioned presently, is quite as good, or rather better. The map represents the spectrum as seen with the lens of 12 inches focal length in front of the prisms. The breadth of the slit was not always quite the same: it may be estimated at about the  $\frac{1}{20}$ th of an inch. The map contains 32 fixed lines or bands more refrangible than H, which is the utmost that I have been able on different occasions to see with this lens, though with a lens of longer focus and a narrower slit the number of fixed lines which might be counted was, as might be expected, a good deal larger. As I have not yet identified these lines, except in certain cases, with those which had previously been represented by means of photographic impressions, I have thought it advisable not to attempt an identification, but to attach letters to the more conspicuous lines in my map without reference to former maps. As the capitals L, M, N, O, P have already been appropriated to designate certain fixed lines, I have made use of the small letters *l*, *m*, *n*, *o*, *p*, to prevent confusion.

In drawing the map, I have endeavoured to preserve the character of the lines with respect to blackness or faintness, sharpness or diffuseness. The distances were not laid down by measurement, except here and there, and they are not, I fear, quite so accurate as might be desired; still, I feel assured that no one viewing the actual object would feel any difficulty in identifying the lines with those in my map, provided the circumstances under which his spectrum was formed at all approached to those under which mine was seen when the arrangement as to focal length of the lens, &c. was that most convenient for general purposes.

The more conspicuous lines in the part of the spectrum represented in the map may conveniently be arranged in five groups, which I will call the groups H, *l*, *m*, *n*, *p*. The group H consists chiefly of the well known pair of bands of which the first contains FRAUNHOFER's line H; the second band I have marked *k*, in accordance with

Professor DRAPER's map. The most conspicuous object in the next group consists of a broad dark band, *l*. This band is between once and twice as broad as *H*, and is darker in the less refrangible half than in the other. With a lens of 3 feet focal length and a narrow slit it was resolved into lines, which is probably the reason why it is altogether omitted in Professor DRAPER's map, while the first three lines of the group (if I do not mistake as to the identification) are represented, forming his group *L*. Under the circumstances to which the accompanying map corresponds, the band *l* appears as a very striking object, perhaps, with the exception of the bands *H*, *k*, the most conspicuous in the whole spectrum. With a still lower power it appears as a very black and conspicuous line. A double line beyond *l* completes the group *l*, after which comes another remarkable group *m*, consisting of five lines or bands. Of these the first is rather shady, though sharply cut off on its more refrangible side, but the others, and especially I think the second and third, are particularly dark and well-defined. I have marked the middle line *m*, not because it is more conspicuous than its neighbours, but on account of its central situation. After a very faint group, consisting apparently of four lines, comes another very conspicuous group *n*, consisting of two pairs of dark bands followed by another pair of bands which are broad and very dark. The first of these is a good deal broader than the second, but is not so broad as the band *H*; the second is followed by a fine line. This is as far as it is easy to see; but when the sunshine is clear, and the arrangements are made with a little care, a group of six lines is seen much further on. Of these, the first two are only moderately dark, and the first is rather diffuse; they stand off a little from the others, and are a little closer together than the other four. Of the latter, the first, marked *o*, is very strong, considering the faintness of the light which it interrupts; the second and third are faint, and difficult to see; the fourth, marked *p*, is black like the first, and a good deal broader. The line *p* was situated, by measurement, as far beyond *H* as *H* beyond *b*. Once or twice in the height of summer, and under the most favourable circumstances, I have observed two broad dusky bands still further on. The first of these had the appearance of being resolvable into two. The excessively faint light seen beyond the second seemed to end rather abruptly at the distance represented by the border of the accompanying plate, as if there were there the edge of another dark band beyond which nothing could be seen. In order to see the dusky bands last mentioned, and even to see the group *p* to most advantage, it was necessary to allow the central part of the beam incident on the prisms to pass through them close to their edges, so that evidently a great deal of light was lost by passing by the prisms altogether. This circumstance, combined with others which I have observed, convinces me that the great obstacle to seeing the fixed lines in this part of the spectrum consists in the opacity of glass. Were glass as transparent with respect to the invisible rays of very high refrangibility as it is with respect to the rays belonging to the visible spectrum, I know not how much further I might have been able to see.

I have endeavoured to identify the fixed lines in my map with the fixed lines represented in M. SILBERMANN'S map of the chemical spectrum, with a copy of which my friend Professor THOMSON has kindly furnished me. I am still uncertain respecting the identification. M. SILBERMANN'S map is so very much more detailed than my own, and must have been made with so much purer a spectrum, that the two systems of lines are not directly comparable.

23. From the difficulty of identification some persons might be disposed to imagine that the chemical rays, and those which produced the blue light in a solution of quinine, were of a different nature, and had each a system of fixed lines of its own. For my own part, I was too well acquainted with the Protean character of fixed lines to regard the difficulty of identification as any valid argument in support of such a view. And that this difficulty arose from nothing more than the different degrees of purity of the spectra is now put past dispute, for my friend Mr. KINGSLEY of Sidney Sussex College, to whom I recently showed some of the experiments mentioned in this paper, has kindly taken for me some photographs of spectra having nearly the same degree of extent and purity as those with which I worked, and these show the fixed lines just as they appeared in a solution of sulphate of quinine and in other media\*.

24. The position of a point in the spectrum which does not coincide with one of the principal fixed lines, will be denoted by referring it to two of those lines, in a manner which will be most easily explained by an example. Thus  $\frac{1}{2}GH$ ,  $G\frac{1}{2}H$ ,  $GH\frac{1}{2}$  will be used to denote respectively a point situated at a distance below G equal to half the interval from G to H, a point midway between G and H, and a point situated at the same distance above H. In using this notation, the letters denoting fixed lines will be written in the order of refrangibility, and the fraction expressing the part of the interval between these lines, which must be conceived to be measured off in order to reach the point whose position it is required to express, will be written before, between, or after the letters, according as the measurement is to be taken from the first line in the negative direction, from the first line in the positive direction, or from the second line in the positive direction, the positive direction being that of increasing refrangibility.

25. From the experiments already described, it appears that the beam of dispersed light which was observed in the experiments of Sir DAVID BREWSTER consisted of two very distinct portions, one arising merely from light reflected from motes, and the other having a far more remarkable origin. It will be convenient to have names for these two kinds of dispersion, and I shall accordingly call them respectively *false internal dispersion* and *true internal dispersion*, or simply *false dispersion* and *true dispersion* when the context sufficiently shows that internal dispersion is spoken of. When dispersion is mentioned without qualification, it is to be understood of true dispersion. Now that it appears that the mere reflexion of light from solid particles held in mechanical suspension has nothing to do with that remarkable kind of internal

\* See note A at the end.

dispersion which is characterized by the "*quaquaversus* polarization," the phenomenon of false dispersion ceases to be of much interest in an optical point of view; while on the other hand the phenomenon of true dispersion, which had always been very remarkable, is now calculated to excite a great additional interest. It will be convenient to mention here the principal characters by which true and false dispersion may be distinguished, although it will be anticipating in some measure the results of observations yet to be described.

26. In true dispersion the dispersed light has a perfectly continuous appearance. In false dispersion, on the other hand, it has generally more or less of a sparkling appearance, and on close inspection is either wholly resolved into bright specks, or so far resolved as to leave on the mind the impression that if the resolution be not complete it is only for want of a sufficient magnifying power.

In true dispersion the dispersed light is perfectly unpolarized. In false dispersion, on the contrary, at a proper inclination the light is almost perfectly polarized in the plane of reflexion.

In false dispersion, which is merely a phenomenon of reflexion, the dispersed light has of course the same refrangibility as the incident light. In true dispersion heterogeneous dispersed light arises from a homogeneous beam incident on the body by which the dispersion is produced.

27. In those bodies, whether solid or liquid, which possess in a high degree the power of internal dispersion, the colour thence arising may be seen by exposing the body to ordinary daylight, looking at it in such a direction that the regularly reflected light does not enter the eye, and excluding transmitted light by placing a piece of black cloth or velvet behind, or by some similar contrivance. It has been usual to speak of the colour so exhibited as displayed by reflexion. As however the cause now appears to be so very different from ordinary reflexion, it seems objectionable to continue to use that term without qualification, and I shall accordingly speak of the phenomenon as *dispersive reflexion*\*. Thus dispersive reflexion is nothing more than internal dispersion considered as viewed in a particular way.

28. The tint exhibited by dispersive reflexion is modified in a peculiar manner by the absorbing power of the medium. In the first place, the light which enters the eye in a given direction is made up of portions which have been dispersed by particles situated at different distances from the surface at which the light emerges. The word *particle* is here used as synonymous, not with *molecule*, but with *differential element*. If we consider any particular particle, the light which it sends into the eye has had to traverse the medium, first in reaching the particle, and then in proceeding towards the eye. On account of the change of refrangibility which takes place in dispersion, the effect of the absorption of the medium is different for the two portions of the whole path within the medium, so that this effect may be regarded as a function of

\* I confess I do not like this term. I am almost inclined to coin a word, and call the appearance *fluorescence*, from fluor-spar, as the analogous term *opalescence* is derived from the name of a mineral.

two independent variables, namely, the lengths of the path before and after dispersion; whereas, had the light been merely reflected from coloured particles held in suspension, the effect of absorption would have been a function of only one independent variable, namely, the length of the entire path within the medium.

29. When false dispersion abounds in a fluid, it may be detected at once by the eye, without having recourse to any of the characters already mentioned whereby it may be distinguished from true dispersion. When a fluid is free from false dispersion it appears perfectly clear, when viewed by transmitted light, although it may be highly coloured, and may even possess to such an extent the property of exhibiting true internal dispersion as to display, when properly viewed, a copious dispersive reflexion. On the contrary, when false dispersion abounds, the fluid, if not plainly muddy, has at least a sort of opalescent appearance when viewed by transmitted light, which, after a little experience, the eye in most cases readily recognises. In viewing the phenomenon of dispersive reflexion, as exhibited in a fluid, it might be supposed that the fluid was water, or else some clear though coloured liquid, holding in suspension a water colour in a state of extreme subdivision. But on holding the fluid before the eye, so as to view it by transmitted light, or rather view a bright well-defined object through it, the illusion is instantly dispelled. The reason of this difference appears to admit of easy explanation, and will be noticed further on.

30. Light will be spoken of in this paper as *active* when it is considered in its capacity of producing other light by internal dispersion. A medium will be said to be *sensitive* when it is capable of exhibiting dispersed light under the influence of light (visible or invisible) incident upon it. In the contrary case it will be called *insensible*.

I shall now return to the description of the appearances exhibited by some of the media most remarkable for their sensibility.

*Decoction of the Bark of the Horse-Chestnut (Æsculus hippocastanum).*

31. In Sir JOHN HERSCHEL's second paper it is stated that esculine possesses in perfection the peculiar properties which had been found to belong to quinine. Having tried without success to procure the former alkaloid, I was content to let this substance pass, till I found how admirably a mere decoction or infusion of the bark of the tree answered for all purposes of observation.

This medium is even more sensitive than a solution of sulphate of quinine, and disperses like it a blue light. The description of the mode of dispersion in the latter medium will apply in almost all points to the former: the principal difference consists in the circumstance that in the horse-chestnut solution the dispersion begins earlier in the spectrum than in the solution of quinine. In a solution of sulphate of quinine of convenient strength, we have seen that the dispersion came on at about  $G\frac{1}{2}H$ , the excessively faint dispersion which was exhibited earlier being left out of consideration, whereas in a decoction of the bark of the horse-chestnut, diluted so as to be



of a convenient strength, it came on a little before G. This explains the reason of an observation of Sir DAVID BREWSTER's, who has remarked that "a beam of light that has passed through the esculine solution disperses blue light, but not copiously, when transmitted through the quinine solution ; but the beam that has passed through quinine is copiously dispersed when transmitted through esculine\*."

*Green Fluor-Spar from Alston Moor.*

32. It is well known that some specimens of fluor-spar exhibit a sort of double colour. In particular, a variety found at Alston Moor, which is green when seen by transmitted light, appears when viewed in a certain manner of a beautiful deep blue. This blue colour seems to have been considered by Sir JOHN HERSCHEL as merely superficial. It has been shown however by Sir DAVID BREWSTER to arise from light dispersed in the interior of the crystal, and to have no particular relation to the surface.

The crystal with which the following observations were made was of a fine but not intense green when viewed by transmitted light. On viewing a pure spectrum through it, there was found to be a dark band of absorption in the red. This band was narrow, and by no means intense. The crystal exhibited a copious deep blue by dispersive reflexion.

33. On admitting into the crystal a cone of sunlight formed by a lens of short focus, and then analysing the dispersed beam, it was found to consist of a very little red followed by a dark interval, then green, faintly fringed below with less refrangible colours down perhaps to the orange, then blue, or bluish-green, followed by a great deal of indigo or violet. Independently of the gap in the red, the spectrum was not quite continuous, for a band of bluish-green, not very broad, was separated by dusky bands from the green below and the indigo above. The separate red band and the two dusky bands were all so faint as to be difficult to see.

The dispersed beam was readily proved to be truly dispersed, for it was unpolarized, and a pale brown glass cut it off when placed in the first position, although it transmitted it in a great measure when placed in the second.

34. When the crystal was examined by the third method, the general result closely resembled that produced by sulphate of quinine. The dispersion commenced about half-way between G and H, and continued from thence onwards far beyond H. It was strongest about H. The fixed lines were seen with beautiful distinctness as dark planes in the crystal. The groups H, *l*, *m* were quite evident, and *n* might be seen without difficulty. I have even seen some of the fixed lines of the group *p*. The tint of the dispersed light appeared as nearly as possible uniform throughout. The distance to which this light could be traced from the surface, did not at all diminish so rapidly in this crystal, with an increase in the refrangibility of the incident light,

\* Philosophical Magazine, vol. xxxii. (June 1848), p. 406.

as it had done in the case of a solution of sulphate of quinine. Indeed, it was difficult to say how far the decrease in the depth to which the incident rays could be traced, by means of the dispersed light which they produced, was due merely to the increasing faintness of the light, and how far it indicated a real increase in the absorbing energy of the crystal; whereas in the case of sulphate of quinine the appearance presented unequivocally indicated a very rapid increase of absorbing power.

35. On examining the crystal by the second method, the general appearance was the same as in the case of sulphate of quinine, but the beam of falsely dispersed light was absent. In addition to the copious beam of deep blue light dispersed by the most refrangible rays, there was however a faint beam of red or reddish light dispersed by rays of low refrangibility. This beam was too faint to be seen by the third method of examination. It will be remembered that the prismatic analysis of the transmitted light gave a band of absorption in the red. Another crystal of a pale colour, which did not give a similar band of absorption in the red, exhibited nothing but the blue beam of dispersed light when examined by the second method.

36. On examining the crystal by the fourth method, the extreme red proved inactive. The activity commenced about the most refrangible limit of the red transmitted by a deep blue glass, when the dispersed light was red, but extremely faint. On moving the lens onwards through the spectrum, the dispersed light rapidly became brighter, and then died away. When at its brightest, although even then it was almost too faint for prismatic examination, it appeared to consist of not quite homogeneous light a little lower in refrangibility than the active light. For a considerable distance further on there was no sensible dispersion produced. The dispersed light became again perceptible when the active light belonged to the greenish yellow, or not till the blue, according to the intensity of the incident light. As the lens moved on the dispersed light remained faint for a considerable time. It was first reddish and then brownish, with a refrangibility answering to its colour. When the active light was at  $G\frac{1}{2}H$ , or thereabouts, the dispersed light rapidly grew much brighter, and became of a fine blue. On analysis it was found to consist of rays the refrangibility of which ranged within wide limits. The red rays were, however, almost wholly wanting, while the rays belonging to the more refrangible part of the spectrum resulting from the analysis of the dispersed beam were particularly copious. The most refrangible limit of the dispersed light did not quite reach in refrangibility the active light. The dispersed light was most copious when the active light belonged to the neighbourhood of  $H$ . As the lens moved on the dispersed light grew less bright, and gradually died away.

*Solution of Guaiacum in Alcohol.*

37. This is one of the media mentioned by Sir DAVID BREWSTER, who remarks that it "disperses, by the stratum chiefly near its surface, a beautiful violet light."

When this fluid is examined by the third or fourth method, it is found to exhibit a copious internal dispersion, which begins to be conspicuous much lower down in the spectrum than in the cases already described. In observing by the third method, the true dispersion appeared to commence about the end of the green, the dispersed light being reddish-brown. By the fourth method the dispersion could be traced as low down as  $D\frac{1}{3}b$ , the dispersed light being reddish. As the lens moved onwards, in a direction from the red to the violet, the more refrangible colours entered in succession into the dispersed beam, and it became successively brownish, yellowish, greenish, and bluish. In whatever part of the spectrum the lens might be, it was found that the most refrangible part of the dispersed beam was of lower refrangibility than the active light. This could be easily determined by means of the beam of falsely dispersed light, which was always visible so long as the active light belonged to the visible part of the spectrum.

38. With the third arrangement the fixed lines were seen as before by means of the dispersed light, but in this fluid they could be seen much lower down in the spectrum than in the solution of sulphate of quinine. The group H was seen on a greenish ground. About the group *l* the ground was still greenish, but the dispersed light was not very copious. The beautiful violet light mentioned by Sir DAVID BREWSTER is produced only by rays of extremely high refrangibility, and is found to extend from the beginning of the group *m* to the end of the group *n*, and even further. This part of the dispersion is best seen with a rather dilute solution.

39. In a solution of guaiacum, just as in the solution of sulphate of quinine, the absorbing power of the medium increases very rapidly with the refrangibility of the light. This is shown by the rapid decrease in the distance from the surface to which the dispersed light can be traced. The reason why the violet dispersed light is confined to a very thin stratum adjacent to the surface by which the light enters, is simply that the medium is so nearly opaque with regard to the invisible rays beyond the extreme violet that all such rays are absorbed by the time the light has passed through a very thin stratum of the fluid.

40. If the solution be strong the colour is of considerable depth. In all such cases it is necessary to take the precaution, mentioned by Sir DAVID BREWSTER, of transmitting the incident beam as near as possible to the upper surface, so as just to graze it. The absorption of the medium would otherwise modify the tint of the dispersed beam.

41. The solutions of quinine and guaiacum present a striking contrast with respect to the change of tint of the dispersed beam. In the former solution the change is but slight, if we except that part of the dispersion which is very faint; whereas in the latter, the prismatic colour which makes the nearest match to the composite tint of the dispersed beam runs through nearly the entire spectrum, as the refrangibility of the active light changes from that of the green rays to that of invisible rays situated far beyond the extreme violet.

*Tincture of Turmeric.*

42. This fluid is very sensitive, and exhibits a pretty copious dispersive reflexion of a greenish light. In its mode of internal dispersion it strongly resembles a solution of guaiacum, but the final tint of the dispersed light does not correspond to so high a mean refrangibility. When the fluid was examined by the third method, the true dispersion appeared to commence about *b*. The absorbing power was so great for the rays of high refrangibility, that from a little above F (in the case of tincture not diluted with alcohol) to the end the dispersed light seemed to be confined to the mere surface. By the fourth method the dispersion was as usual traced a little lower down in the spectrum. When the dispersed beam was first perceived it was nearly homogeneous, and its refrangibility was only a very little less than that of the active light. As the refrangibility of the active light increased, new colours, in the order of their refrangibility, entered into the dispersed beam, which became more and more composite, while at the same time its upper limit became distinctly separated from the beam of falsely dispersed light, which, when the whole dispersed beam was analysed by a prism, was always found in advance of the other. The tint of the dispersed beam passed from orange through yellow to yellowish green, which was its final tint. Tincture of turmeric is well adapted for exhibiting the fixed lines in the invisible part of the spectrum, though perhaps not quite so well as a solution of sulphate of quinine.

*Alcoholic Extract from the Seeds of the Datura Stramonium.*

43. This fluid, which I was led to try in consequence of Sir DAVID BREWSTER'S paper, proved to be remarkably sensitive, and exhibited a copious dispersive reflexion of a pale but lively green. The general phenomena are so nearly the same as in a solution of sulphate of quinine that there is no need of a separate description. The principal difference consists in the tint, which is green instead of blue. In the present case, however, the fluid, in addition to its dispersion of green, dispersed a red beam under the influence of certain red rays. As the lens employed in the fourth method of examination was moved from the extreme red onwards, the light was at first inactive, but when the lens reached a certain point of the spectrum, a red beam of truly dispersed light suddenly appeared, which disappeared with almost equal suddenness as the lens moved on. In this mode of observation the refrangibility of the dispersed could hardly be distinguished from that of the active light; but on combining the first and third methods, by removing the lens, placing the vessel truly in focus, and holding a blue glass alternately in front of the vessel and in front of the eye, I satisfied myself that the truly dispersed beam, taken as a whole, was of lower refrangibility than the light by which it was produced. The utility of the blue glass depended upon the circumstance that the upper extremity of the extreme red which it transmitted nearly coincided with the point of the spectrum at which the red beam occurred. This red beam was doubtless due to the presence of a small quantity of

chlorophyll, or one of its modifications. The light transmitted by the fluid exhibited on prismatic analysis the absorption band in the red which is so characteristic of that substance.

The colour of the solution was a pale brownish yellow; it would no doubt have been still paler, and perhaps nearly colourless, had the sensitive principle to which the green dispersion was due been present in equal quantity but in a state of purity. As it was, the fluid was pale enough to exhibit well, when poured into a test tube and held in front of a window, a narrow arc on the side of the incident light, like sulphate of quinine, only in this case the arc was green instead of blue.

*Frequency of the occurrence of true internal dispersion having the same general character as that which takes place in the cases above described.*

44. If we except the red dispersed beam produced by red rays in the crystal of fluor-spar and in the stramonium extract, a strong similarity may be observed in the mode of internal dispersion which takes place in the cases hitherto described. As the refrangibility of the incident light continually increases, the rays are at first inactive. At a certain point of the spectrum, varying according to circumstances, the true dispersion begins to be sensible, but is faint at first. After remaining faint for some distance it presently becomes more copious. It remains very conspicuous through the whole of the violet and beyond, and then gradually dies away. It consists at first of light of comparatively low refrangibility, and then new colours in the order of their refrangibility enter into it. Frequently the greater part of the change of prismatic composition takes place while the dispersed light is very faint, so that practically speaking we may almost say that the tint is uniform. Sometimes, when the dispersion just commences, the dispersed light is nearly homogeneous, and has a refrangibility so nearly equal to that of the active light that the beams due to true and false dispersion can hardly be separated.

45. Now this, so far as I have observed, is much the commonest kind of true internal dispersion, although sometimes the phenomenon presents very striking singularities. In the paper in which Sir DAVID BREWSTER first announced the discovery of internal dispersion, he remarks "that it is a phenomenon which occurs almost always in vegetable solutions, and almost never in chemical ones or in coloured glasses\*." For my own part, I have rarely met with a vegetable solution which did not exhibit more or less the phenomenon of *true* internal dispersion. Its existence may in general be easily detected in the following manner. The sun's light being reflected horizontally through a lens, a deep blue glass is left in such a position as to intercept the light incident on the vessel containing the fluid, which is placed at the focus of the lens. A pale brown glass of the proper kind is then placed so as to intercept, first the incident, and then the dispersed light. A vessel with flat sides filled with a solution of sulphate of quinine would be better, and then the placing of the

\* Edinburgh Transactions, vol. xii. p. 542.

medium in the second position might be dispensed with, the medium being sensibly transparent. Sometimes it is useful to have recourse to analysis through a doubly refracting prism, or a rhomb of calcareous spar. In this way true internal dispersion may often be detected in a fluid which is actually muddy, in which case, were the effect of the incident light observed as a whole, the true would be masked by the enormous quantity of false dispersion which such a medium would offer.

46. The fluids obtained by treating the leaves and other parts of plants with alcohol or hot water are almost always sensitive, so far as I have observed. The solutions in water presently ferment, and are frequently highly sensitive in the early stages of fermentation; they are usually more or less sensitive in all stages. Different kinds of fungus furnish very sensitive solutions. When aqueous solutions become muddy by decomposition, other clear and often highly sensitive liquids may be obtained from them by various chemical processes. Port and sherry are decidedly sensitive. In such cases the fluid is a mixture of several substances, of which some may be sensitive and others insensible. When vegetable substances are isolated they are frequently insensible, or else so very slightly sensitive when examined under great concentration of the highly refrangible rays, that it is quite impossible to say whether the sensibility thus exhibited may not be due to some impurity: thus, several solutions containing sugar, salicine, morphine, or strychnine were found to be insensible. A solution of veratrine in alcohol proved to be sensitive in a pretty high degree, dispersing internally a bluish light. Sir DAVID BREWSTER has remarked that a solution of sulphate of strychnine in alcohol dispersed light *after it had stood for some days*. This observation I have verified with reference to *true* dispersion, which the solution exhibits, though not very copiously, after it has been made some time. There can be little doubt that the sensitive principle in this case is not strychnine, but some product of its decomposition. I now come to some instances of internal dispersion which are far more striking.

#### *Solution of Leaf-Green in Alcohol.*

47. It was in this very remarkable fluid that the phenomenon of internal dispersion was first discovered by Sir DAVID BREWSTER, while engaged in researches relating to absorption. The character of the internal dispersion of a solution of leaf-green is no less remarkable than the character of its absorption. On account of the close connexion which seems to exist between the two phenomena, it will be requisite first to say a few words about the latter.

When green leaves are treated with alcohol, a fluid is obtained which is of a beautiful emerald-green in moderate thicknesses, but red in great thicknesses, and which has a very remarkable effect on the spectrum. A good number of the following observations on the internal dispersion of leaf-green were made with a solution obtained from the leaves of the common nettle, by first boiling them in water and then treating them with cold alcohol, the leaves having previously been partially

dried by pressing them between sheets of blotting paper. Nettle was chosen partly because it stands boiling without losing its green colour, and partly for other reasons. My object in boiling the leaves was to obtain the green colouring matter more nearly in a state of isolation, but it seems to have the additional advantage of giving a solution less liable to decomposition. Indeed, this fluid seemed disposed to remain permanently unchanged when kept in the dark; but a small portion of it which was exposed to strong light had its colour rapidly discharged.

48. When fresh leaves are left in contact with alcohol in the dark, or in only weak light, the colour of the fluid changes by degrees, and it seems to approximate (making allowance for impurities) to a type which is nearly represented by the fluid obtained in this manner from laurel leaves, or that obtained by treating with alcohol tea leaves from which a good deal of brown colouring matter has first been extracted by water. This type was rather ideal than actual, being derived from a comparison of different cases, until it seemed to be realized in the case of a fluid obtained by re-dissolving in alcohol a crust which had formed itself at the bottom of a test tube containing leaf-green. The principle to which the peculiar absorption and internal dispersion of such a fluid seems due may be called modified leaf-green. The fluid itself is not green but olive-coloured, becoming red at great thicknesses.

49. When solutions of leaf-green, and of its various modifications, are examined in different thicknesses by the light of a candle, there are five bands of absorption which may be observed in the spectrum. These will be called, in the order of their refrangibility, Nos. 1, 2, 3, 4 and 5, the bright bands below the respective dark bands being also numbered in the same manner. Of the dark bands, Nos. 1, 2, 3 and 5, are the first four in Sir DAVID BREWSTER'S plate\*. No. 4 is mentioned in the memoir, but not represented in the plate, which corresponds to a thickness not sufficient to bring out this band. The last band in the plate could not be seen without strong light. The dark bands Nos. 1 and 2 are situated in the red, No. 3 about the yellow or greenish yellow, No. 4 in the green, and No 5 early in the blue. Of these, No. 1 is in small thicknesses by far the most intense, and it may be readily seen even in a very dilute solution; it might apparently be used as a chemical test of chlorophyll, or one of its modifications. The test would be of very easy application, since it would be sufficient to hold a test tube with the liquid at arm's length before a candle at a little distance, and view the linear image of the flame through a prism applied to the eye.

50. Fresh and modified leaf-green differ much in the order in which the bright bands are absorbed, and in the degree to which the dark bands are developed before they cease to be visible by the absorption of the part of the spectrum in which they are situated. In the green fluid, the dark band No. 5 is not usually seen, because the spectrum is there cut off, unless a very small thickness be used. With a moderate thickness, Nos. 2 and 3, especially the former, are well seen, and No. 1 is very intense. As the absorption goes on, the bright bands Nos. 2 and 3 are absorbed,

\* Edinburgh Transactions, vol. xii.



and there is left the red band No. 1, and a double green band, consisting of the bright bands Nos. 4 and 5, separated by the dark band No. 4, which by this time has come out. In modified leaf-green, the dark bands Nos. 4 and 5 are much more conspicuous than in the green fluid, but No. 3 is wanting, or all but wanting. With a thickness by which the absorption is well developed, the conspicuous bright bands are in this case Nos. 1 and 3, and next to them No. 2, whereas in the green fluid Nos. 2 and 3 were quickly absorbed, or at least the whole of No. 2, and the greater part of No. 3.

51. It seems worthy of remark, that, especially in the case of the green fluid, the absorbing power alters with the refrangibility of the light at a very different rate on the two sides of the intense dark band No. 1. This might be inferred from the order in which the bright bands disappear; but it was rendered visible to the eye by the following easy experiment. A narrow test tube was partly filled with a solution of leaf-green, and then a few drops of alcohol were added, which remained at the top, and there diluted the solution. The tube was then held before a candle, and the linear image of the flame was viewed through a prism. In the under part the dark band No. 1 was broad, the bright band No. 2 being narrow, and almost obliterated, but in the upper part the dark band No. 1 was very narrow. Now on tracing upwards the sides of this dark band, it was found that the less refrangible side was almost straight, and the diminution in the breadth of the band was produced by the encroachment of the bright band No. 2. Speaking approximately, we may say that in proceeding from the extreme red onwards, at a certain point of the spectrum the fluid passes abruptly from transparent to opaque, and then gradually becomes almost transparent again.

52. It may here be remarked, that although the absorption produced by leaf-green is best studied in a solution, its leading characters may be observed very well by merely placing a green leaf behind a slit, as near as possible to the flame of a candle, and then viewing the slit through a prism.

53. After this digression relating to the absorption of leaf-green, it is time to come to its internal dispersion. And first, when a cone of white light coming from the sun is admitted horizontally into the fluid, as close as possible to its upper surface, and the beautiful red beam of dispersed light is analysed by a prism, the spectrum is found to consist of a bright red band of a certain breadth, followed by a dark interval, and then a much broader green band not near so brilliant. There is usually but little false dispersion, and what there is may be almost entirely got rid of by analysing the beam by a Nicol's prism, so as to view it by light polarized in a plane perpendicular to the plane of dispersion. Now on raising the vessel without removing the prism from the eye, it was found that a dark band, which was in fact the absorption band No. 1, appeared almost exactly in the middle of the bright red band. On continuing to raise the vessel, so as to make the dispersed rays pass through a still greater thickness of the medium before reaching the eye, the dark

band increased in width, and when the red beam was almost absorbed, the part that was left consisted of two cones of red, one at each side of the dark band, which by this time had become broad. The whole appearance seemed to indicate that the bright red beam of dispersed light had a very intimate connexion with the intense absorption band No. 1.

54. Among coloured glasses, there is one combination which produces a very striking effect. When a deep blue glass is placed in the first position, the dispersed light, if the solution be at all strong, is confined to a very thin stratum adjacent to the surface, and is best seen by placing the vessel so that the surface of the fluid at which the light enters is situated at a little distance on either side of the focus of the lens, when there is seen a bright circle of a most beautiful crimson colour. It might be supposed that the red of which this circle mainly consists was nothing but the extreme red transmitted by the blue glass. But it is readily shown that such is not the case. For in the first place, the fluid transmits pretty freely the red transmitted by the blue glass, whereas the red light found in this circle is almost confined to the surface of the fluid. Again, it was found that a pale brown glass, which transmitted freely the extreme red, almost entirely cut off the bright circle, when placed in the first position without removing the blue glass, although it freely transmitted it when placed in the second position. It appears, therefore, that the bright circle is due, not to the red, but to the highly refrangible rays transmitted by the blue glass.

55. When a solution of leaf-green was examined by the third method, the appearance as seen from the outside was very singular. The fixed lines in all the more refrangible part of the spectrum were seen as interruptions in a bright red ground verging to crimson. The beauty and purity of the tint, and the strange contrast which it presented to the colours belonging to that part of the spectrum, were very striking. About H the tint began to verge towards brown, and the fixed lines beyond H were seen on a brownish red ground. That the ground on which the fixed lines of somewhat less refrangibility were seen was rather crimson than red, arose, no doubt, from the mixture of a little blue or violet light due to false dispersion, and to the scattering which took place at the surface of the glass.

56. On looking down from above, the places of the more conspicuous bands of absorption were indicated by dark teeth, with their points turned towards the incident light, interrupting the dispersed light. It is to be understood that the light was transmitted as close as possible to the upper surface, so that the absorption by which these teeth were formed took place *before* dispersion. In this way the places of the absorption bands Nos. 1, 2 and 4, were perfectly evident. No. 3, it will be remembered, was by no means conspicuous. When the solution is of convenient strength, the absorption is so rapid beyond the bright band No. 5, that the dispersion is confined to a thin stratum close to the surface by which the light enters, and therefore no dark tooth would be seen corresponding to the dark band No. 5.

57. On following the active light through the spectrum, in the direction of increasing refrangibility, the dispersion was found to commence with a bright, but narrow tail of pure red light, which shot right across the vessel. The light by which this tail was produced belonged to the more refrangible part of the extreme red band which is transmitted by a moderate thickness of the fluid. The activity of the incident light commenced almost abruptly: the same, it will be remembered, was the case with the absorbing power of the medium. After the tail of red light came the intense absorption band No. 1, where the dispersed light was confined to the immediate neighbourhood of the surface by which the active light entered. At this place a very bright band of dispersed light was visible on looking at the vessel from the outside. In this part of the spectrum the active and the dispersed light were both red; but that dispersion was accompanied by a change of refrangibility, was shown by the effect of absorbing media. Thus the long red tail and the bright band adjacent to the surface were differently affected by a blue glass, according as it was held in the first or the second position; and the bright band, though much enfeebled, was still plainly visible through a considerable thickness of the fluid, although a stratum having a thickness of only a very small fraction of an inch was sufficient to absorb the rays by which the band was produced. Although the dispersion continued throughout the whole of the visible spectrum and beyond, it was comparatively feeble in the brightest part of the spectrum. It became pretty copious again in the neighbourhood of the dark band No. 4, and remained copious throughout the blue and violet. In the green, the dispersed light was red, slightly verging towards orange, and in the blue and violet it was red verging a little towards brown.

58. It may seem superfluous, after what precedes, to bring forward any further proof of the reality of a change of refrangibility. Nevertheless the following experiment, which was in fact performed at an early stage of these researches, may not be deemed wholly unworthy of notice, as not involving the use either of absorbing media or of false dispersion.

A small narrow triangle of white paper was stuck on to the outside of the vessel containing the leaf-green, in such a manner that its axis was vertical, and its vertex, which was uppermost, was situated at the height of the middle of the spectrum. A narrow vertical slit was then placed at the distance of the image of the first slit, where the fixed lines were formed, and moved sideways till the light immediately beside the fixed line G passed through it. The vessel was then placed a few inches behind the slit, and moved sideways till the riband-shaped beam of homogeneous light, which passed through the second slit, was incident on the vertex of the triangle. On looking at the vessel from the front, as nearly as was convenient in the direction of the incident light, there appeared a bright vertical bar corresponding to a section of the incident beam. This bar was of two colours, namely, red in the upper half, where the light fell on the fluid, and indigo in the under half, where it fell on the paper. On refracting the whole system sideways,

through a prism of moderate angle applied to the eye, the objects appeared in the following order as regards refrangibility. First came the upper half of the bright bar, which was only a very little widened by refraction, so that it consisted of red light which was approximately homogeneous. Next came the triangle, with its vertex a little rounded, and its edges tinged with prismatic colours. The vertex, which had formerly coincided with the bright bar, now lay a little to one side of its upper half. The triangle was of course seen by means of the diffused light of the room, which was not perfectly dark, and therefore its refrangibility must have corresponded to the brightest part of the spectrum, or nearly so. Lastly came the under half of the bright bar, which was much more refracted than the triangle, so as to be shifted almost completely off it. The paper triangle was far too close to the first surface of the fluid to allow of attributing the dislocation of the bright bar to any error depending upon parallax; but to prevent all possible doubts on this score, I took care to refract the system both right and left, and the result was the same in the two cases. The conclusion is therefore inevitable, that the indigo light which had changed its colour by dispersion from leaf-green had changed its refrangibility at the same time.

59. In viewing a solution of leaf-green in a pure spectrum, I noticed a phenomenon which further indicates the close connexion which seems to exist between the absorption and internal dispersion of this fluid. On holding the eye vertically over the fluid, and looking down at the dispersed light through a red glass, I observed five minima of illumination, having for the most part the shape of teeth with their bases situated at the surface by which the light entered, and their points turned inwards. These minima occupied positions intermediate between the bands of absorption, so far at least as the positions of the latter were indicated by dark teeth pointing in the contrary direction. The first minimum was situated a little beyond the intense absorption band No. 1, and corresponded in position to the bright band No. 2. The second was situated a little further on. The maximum intervening between this and the third was but slight, so that the second and third together formed pretty nearly one broad minimum. The third and fourth were situated one at each side of the dark band No. 4, so as to correspond in position to the bright bands Nos. 4 and 5. The fifth was situated a little way beyond the bright band No. 5. This last minimum was not tooth-shaped, inasmuch as it occurred at a part of the spectrum where the dispersed light was almost confined to the surface of the fluid. These minima are best seen when the solution is rather weak. They may be perceived without using a red glass, though not so easily as with its assistance. With a stronger solution it was observed that the first minimum ran obliquely into the dark tooth corresponding to the absorption band No. 1.

60. The reason of the occurrence of these minima appears to be simply this, that the more copiously dispersed light is produced, the more rapidly the incident light is used up in producing it, so that minima of activity correspond to points of the

spectrum at which the incident light penetrates to comparatively great distances into the fluid before it is absorbed. The oblique position observed in the first minimum is readily explained by considering that the illumination at any point of the field of view depends conjointly upon the activity of the incident light, which is a function of its refrangibility, and upon the fraction of the incident light left unabsorbed, which last is a function both of the refrangibility and of the distance from the first surface.

61. It seems worthy of remark, that while the quantity of dispersed light is liable to fluctuations having an evident relation to the bands of absorption which occur throughout the spectrum, the quality of the light dispersed, as regards its refrangibility, appears rather to have reference to the intense absorption band No. 1.

*Extract from blue leaves of the Mercurialis perennis.*

62. The juice of this plant has the property of turning blue by exposure to the air. Some leaves and stalks which had turned blue were treated with alcohol, and a green fluid was thus obtained much resembling in colour the ordinary solutions of leaf-green, but I think of a rather bluer green than usual. In its mode of absorption, too, it much resembled ordinary solutions of leaf-green, to which substance no doubt the greater part of its colour was due. Its internal dispersion however was very peculiar, for it dispersed a copious orange in place of a blood red like the extracts from fresh green leaves in general, those of the *Mercurialis perennis* included. On analysis the dispersed beam was found to consist chiefly of a red band, similar to that which occurs in solutions of leaf-green, and of a yellow or orange and yellow band, a good deal brighter than the former, from which it was separated by an intervening dark band. When the fluid was examined by the second method, it was found that the yellow dispersion was produced principally by the brightest part of the spectrum. After a considerable time the fluid lost its fine green colour, as is very often the case with solutions of leaf-green, and became yellowish brown, but the red and yellow dispersions still continued.

When the fluid was examined by the fourth method, it was found that the red rays dispersed a red, just as in a solution of leaf-green. The additional dispersion which was so conspicuous in this fluid began almost abruptly about the fixed line D. When it was first observed, the refrangibility of the orange dispersed light could hardly, if at all, be separated from that of the active light. As the lens moved on, the orange beam rapidly grew brighter, and yellow entered into it; and now it was easy to see that the beam of falsely dispersed light lay at its more refrangible limit. The orange and yellow dispersed beam was brightest at about  $D\frac{2}{3}E$ ; but though it decreased in intensity it could be traced far beyond that point, in fact, throughout the spectrum.

63. I have generally found that when a copious dispersion commences almost abruptly at a certain point of the spectrum, it is followed by a band of absorption in

the transmitted light. This law did not seem applicable to the orange dispersion exhibited by the solution just mentioned; but then it is to be remembered that the solution contained a quantity of chlorophyll, which produces absorption bands with such energy that it would naturally mask the bands which might be due to another colouring principle with which it was mixed. To try whether the law would be obeyed if the chlorophyll were got rid of, I boiled in water some portions of the root and young shoots which had turned blue, chlorophyll being insoluble in water. The solution thus obtained was red, in small thicknesses pink, and dispersed copiously a yellow or rather orange light. On subjecting the fluid to prismatic analysis, a band of absorption was seen at the place expected. Since aqueous solutions of this nature are liable to decomposition, frequently decomposing before sunlight can be obtained by which to examine them, the red solution was concentrated by evaporation and purified by alcohol, in which the orange-dispersing principle is soluble, as had already appeared from the properties of the alcoholic solution. The alcoholic solution thus obtained remained unchanged, at least for a long time, and had the further advantage over the aqueous solution of presenting the sensitive principle more nearly in a state of isolation, though it was still contaminated by some principle which dispersed a whitish light under the influence of rays of high refrangibility.

64. The blue colouring matter may be readily extracted by cold water, but is decomposed by boiling. The blue solution dispersed an orange light like the other, but the dispersed light could not be nearly so well seen, just as would be the case were the red orange-dispersing fluid mixed with an insensible blue fluid of a much deeper colour, so that the mixture of the two would be blue. And in fact when the blue fluid was changed to red by boiling the colour became far less intense.

#### *Archil and Litmus.*

65. It is stated by Sir DAVID BREWSTER that a very remarkable example of internal dispersion, which had been pointed out to him by Mr. SCHUNK, is exhibited in an alkaline or in an alcoholic solution of a resinous powder produced from orceine by contact with the oxygen of the air. Not being able readily to procure a specimen of orceine, I tried archil, and obtained from it and litmus some very remarkable solutions.

In the fluid state in which archil is sold, the colour is much too deep for convenient optical examination. When a small quantity of archil is diluted with a great deal of water, the diluted fluid is very sensitive. It is red by transmission, or in small thicknesses purple, but exhibits by dispersive reflexion a pretty copious but rather sombre green.

66. When the fluid was examined by different methods, it was found to disperse a little red, some orange, and a great deal of green. The red dispersion was so slight, that in observing by the third method it appeared doubtful whether there was any except false dispersion. It commenced in the red, when the active and dispersed lights had the same refrangibility, or nearly so. The orange dispersion commenced

about the fixed line D, the dispersed light being at first nearly homogeneous, and of the same refrangibility as the active light. On proceeding onwards in the spectrum, in observing by the fourth method, the orange beam became brighter, and yellow entered into it, but no colour beyond that, so that the orange and yellow beam was left behind by the beam of falsely dispersed light, from which it was separated by a perfectly dark interval. The green dispersion began about  $b$ , or a little beyond, coming on almost abruptly. The manner of its commencement was best observed by the fourth method, by holding a prism to the eye while the lens was moved through the spectrum. In this way it was found that on arriving at the point of the spectrum above mentioned, a gleam of green light shot across the dark space which before separated the beam of falsely dispersed light from the orange beam of truly dispersed light. As the lens moved on, the green dispersed light grew brighter, but its more refrangible limit did not seem to pass, or at least much to pass, the refrangibility it had at first; so that the green beam of truly dispersed light was almost immediately left behind by the beam of falsely dispersed light. The former, on being left behind, soon died away.

67. We might suppose either that the red, orange and green dispersions are due to the same sensitive principle, or that they are produced by three distinct sensitive principles mixed together in the solution. The latter would appear the more probable supposition, to judge by the apparent want of connexion between the three dispersions. This view is strongly confirmed by the following results. Some ether was poured on archil in the fluid state, and after being gently moved about and allowed to stand, a little was withdrawn without agitation. A purplish rose-coloured fluid was thus obtained, which was highly sensitive, exhibiting the orange and green dispersions but not the red. The orange dispersion was far more copious, in proportion to the whole quantity of dispersed light, than had been the case with archil diluted with water.

Some archil was violently agitated with ether, and after subsidence the ether was withdrawn. This ethereal solution was much deeper in colour than the former, and exhibited the red dispersion in addition to the orange and green. On adding a small quantity of water, and agitating, a separation, or at least partial separation, of the sensitive principles took place; for the upper fluid exhibited the orange dispersion abundantly, but none of the red, and little or none of the green, while the under fluid exhibited the green and red dispersions with little, if any, of the orange. The upper fluid exhibited a pretty copious dispersive reflexion of reddish orange, and the under fluid a remarkably copious reflexion of a fine green. A similar separation, more or less perfect, took place in other cases, the dispersion of orange bearing to that of green a greater ratio in the ether than in the water. Some of the green-dispersing fluids thus obtained were most remarkable on account of the extraordinary copiousness of the reflected green, and the strange contrast which it presented to the transmitted tint, which was a purplish red.



The red dispersion in the second ethereal solution, though decided, was by no means copious. In the case of archil merely diluted with water, it had been so slight that its existence might have been considered doubtful. It might be supposed that the first solution was not sufficiently concentrated to exhibit the red dispersion, in which case the red and green dispersions might have been due to the same sensitive principle. But an ethereal extract from dried archil, which was plainly concentrated enough, did not exhibit the red dispersion, although it did exhibit the orange and green dispersions. None of the sensitive principles appear to constitute the chief part of the colouring matter of this dye-stuff.

68. When some of these ethereal solutions were examined by the third method, with a lens of shorter focus than usual, the appearance was very singular. At the less refrangible end of the spectrum the incident light was quite inactive; and then, on reaching a certain point, a copious dispersion of orange commenced abruptly. This continued with no particular change for some distance further on, when it passed abruptly into green. The fourth method showed however that the former dispersion continued, and was only masked, in the third method of observation, by a new and more powerful dispersion of green which then commenced. And in fact when the green-dispersing principle was separated, or partially separated, by water, the orange dispersion was seen to continue where before it appeared to have been exchanged for green.

69. I ought here to mention that a similar separation did not take place on the addition of water only to an ethereal extract from archil previously dried. The condition which determined the separation in the first case appeared to be the presence of a small quantity of ammonia, which would evaporate on drying the archil. And in fact when a small quantity of ammonia was added to the extract from dried archil, a partial separation was effected. I do not here enter into the question whether one of the sensitive principles may be obtained from the other, whether, for example, a chemical combination of the orange-dispersing principle with ammonia might disperse a green, or a green with a little orange. A solution containing a mixture of the same substance in two different states of chemical combination, both compounds being sensitive, is not the less justly regarded as containing two distinct sensitive principles.

70. The preceding results are mentioned, not for their own sake, but merely for the sake of the method of examination employed. The results indeed are so imperfect as to be worthless on their own account. A complete optico-chemical examination of archil and litmus would itself alone furnish a subject for research of no small extent; but it belongs rather to chemistry than to general physics. It is quite possible that internal dispersion may turn out of importance as a chemical test. The dispersing such a tint, and the having the dispersed light produced by light of such a refrangibility, form together a double character of so peculiar a nature that it enables us, so to speak, to see a sensitive principle in a solution containing many sub-

stances, some of them, perhaps, coloured, so that the colour of the solution may be very different from what it would be if the sensitive principle were present alone.

71. The law mentioned at the beginning of art. 63 did not seem very applicable to archil when the fluid was merely diluted with water. But when the orange-dispersing and green-dispersing principles were obtained, as it would appear, more nearly in a state of isolation, by means of ether and water, the law was found to be obeyed. Thus, when the ethereal solution which exhibited the orange dispersion and little else was examined by the third method, the dispersion was found to commence with a tail of light followed by a dark tooth, indicating the position of a band of absorption. When the light transmitted by a certain thickness of this fluid was subjected to prismatic examination, it was found to consist of red followed by some orange, when the spectrum was cut off with unusual abruptness. After a broad dark interval came the most refrangible colours faintly appearing. Those solutions which exhibited a copious dispersion of green gave, in addition to a band obliterating the yellow, a very distinct band separating the green from the blue. A similar band, but by no means distinct, might be seen in archil merely diluted; and it is particularly to be observed that this band, which occurred a little above the point of the spectrum where the green dispersion commenced, became more conspicuous when the green-dispersing principle was present more nearly in a state of isolation.

72. Two portions of litmus were treated, one with ether and the other with alcohol, which were allowed to remain in contact with the solid. Both extracts, but especially the latter, were highly sensitive, exhibiting dispersions of orange and green similar to archil, and due apparently to the same sensitive principles. The ethereal extract dispersed chiefly orange, while the alcoholic extract dispersed orange and green in nearly equal quantities. The latter extract exhibited a remarkably copious dispersive reflexion of a colour nearly that of mud, and was altogether one of the strangest looking fluids that I have met with. On viewing it in such a manner that no transmitted light entered the eye, one might almost have supposed that it was muddy water taken from a pool on a road. But when the bottle containing it was held between the eye and a window the fluid was found to be perfectly clear, and of a beautiful purple colour.

#### *Canary Glass.*

73. Among media which possess the property of internal dispersion in a high degree, Sir DAVID BREWSTER mentions a yellow Bohemian glass, which dispersed a brilliant green light. This led me to seek for such a glass, and it proved to be pretty common in ornamental bottles and other articles. The colour of the glass by transmitted light is a pale yellow. Its ornamental character depends in a great measure upon the internal dispersion, which occasions a beautiful and unusual appearance in the articles made of it. The commercial name of the glass is canary glass. The following observations were made with a small bottle of English manufacture.

74. When the sun's light was admitted without decomposition the dispersed beam

was yellowish green. The dispersion was so copious that when a large lens was used the dispersed beam approached to dazzling. The prismatic composition of this beam was extremely remarkable. The beam was found on analysis to consist of five bright bands, which were equal in breadth and equidistant, or at least very nearly so, and were separated by narrow dark bands. The first bright band was red, the second reddish orange, the third yellowish green, the fourth and fifth green. I have very frequently observed dark bands, or at least minima, in the spectrum resulting from the prismatic analysis of dispersed beams, but I have not met with any example so remarkable as this, except in a class of compounds which the properties of canary glass led me to examine.

75. On analysing a beam of sun-light transmitted through a certain thickness of the glass, there was found to be a dusky absorption band a little below F, another less distinct at  $F\frac{1}{2}G$ , and the spectrum was cut off a little below G.

76. When the glass was examined by the third method, the dispersion was found to commence abruptly about the fixed line *b*. It remained remarkably copious throughout the whole of the visible spectrum and far beyond, with the exception of a band beginning a little above F, and having its centre at about  $F\frac{1}{3}G$ , where there was a remarkable minimum of activity. This band, it will be observed, was situated between the bands of absorption already mentioned. The tint of the dispersed light appeared to be uniform throughout, except perhaps where the dispersion was just commencing. This was the best medium I have met with for showing the fixed lines of extreme refrangibility, though some others were nearly as good.

77. On examining the glass by the fourth method, it was found that the dispersion commenced nearly where the dispersed light ended, that is, the lowest refrangibility of the rays capable of being dispersed was nearly the same as the highest refrangibility of the rays constituting the dispersed beam exhibited by white light as a whole. The dispersion appeared indeed to commence a little earlier, at about the refrangibility of the fourth dark band in the spectrum of the entire dispersed beam. When the small prism was held to the eye with one hand, while the small lens in the board was gradually moved with the other, in a direction from the red to the violet, through the part of the spectrum where the dispersion commenced, it was found that the region of the first four bands was lighted up almost simultaneously, the whole field of view having been previously dark. When the lens was moved a very little further on the dispersed beam with its five bands was formed complete. Indeed the whole five appeared almost simultaneously. Speaking approximately, and in fact with almost perfect accuracy, we may say that if white light be conceived to be decomposed into two portions, the first containing rays of all refrangibilities up to that of the fixed line *b*, or thereabouts, and the second containing rays of all greater refrangibilities, the dispersed light produced by white light as a whole belongs exclusively to the first portion; and yet, were the bottle illuminated by the first portion alone, no dispersion whatsoever would be produced, whereas were it illuminated by the second portion

alone, which contains not a ray having the same refrangibility as any one of the dispersed rays, the dispersion would be exhibited in full perfection.

*Common Colourless Glasses.*

78. Sir DAVID BREWSTER states that he has met with many specimens, both of colourless plate and colourless flint glasses, which disperse a beautiful green light. All the colourless glasses which I have examined dispersed light internally to a greater or less extent, with the exception of some few specimens belonging to Dr. FARADAY's experiments. A beautiful green seems to be the commonest tint of the dispersed beam, and this I have found in wine glasses, decanters, apothecaries' bottles, pieces of unannealed glass, &c.; also in many specimens of plate and crown glass. The green was generally of a finer tint than that dispersed by the canary glass, but was not near so copious. On analysis it was found to consist usually of red and green separated by a dark band, or rather a minimum of brightness. Those specimens which were examined by the third and fourth methods were found to exhibit a little false dispersion, produced chiefly in the brightest part of the spectrum, but the greater part was true dispersion. This dispersion was produced chiefly by a rather narrow band, comprising the fixed line G, where there appeared to be a remarkable maximum of sensibility. The line G lay a little above the lower limit of the band. Below the band dispersion also took place, though not near so copiously, and there appeared to be another maximum of sensibility some way further down in the spectrum; but above the band dispersion almost entirely ceased of a sudden; a very unusual circumstance when the active and the dispersed light are well separated in refrangibility. The position of the band in the spectrum, and the distribution of the illumination in it, which are very peculiar, were the same in all the specimens which were sufficiently sensitive to admit of being examined by the third method, but the tint of the dispersed light was not quite the same.

79. Orange-coloured glasses are frequently met with which reflect from one side, or rather scatter in all directions, a copious light of a bluish-green colour, quite different from the transmitted tint. In such cases the body of the glass is colourless, and the colouring matter is contained in a very thin layer on one face of the plate. The bluish green tint is seen when the colourless face is next the eye. As this phenomenon was supposed by Sir JOHN HERSCHEL to offer some analogy with the reflected tints of fluor-spar and a solution of sulphate of quinine, I was the more desirous of determining the nature of the dispersion. It proved on examination to be nothing but false dispersion, so that the appearance might be conceived to be produced by an excessively fine bluish-green powder contained in a clear orange stratum, or in the colourless part of the glass immediately contiguous to the coloured stratum. The phenomenon has therefore no relation to the tints of fluor-spar or sulphate of quinine. It is true that the very same glass which displayed a superficial reflexion of bluish green, when examined by condensed sun-light exhibited also, in its colour-

less part, a little true dispersion, just as another colourless glass would do. But this has plainly nothing to do with the peculiar reflexion which attracts notice in such a glass.

*Observations on the preceding results.*

80. There is one law relating to internal dispersion which appears to be universal, namely, that when the refrangibility of light is changed by dispersion it is *always lowered*. I have examined a great many media besides those which have been mentioned, and I have not met with a single exception to this rule. Once or twice, in observing by the fourth method, there appeared at first sight to be some dispersed light produced when the small lens was placed beyond the extreme red. But on further examination I satisfied myself that this was due merely to the light scattered at the surfaces of the large prisms and lens, which thus acted the part of a self-luminous body, emitting a light of sufficient intensity to affect a very sensitive medium.

81. Consider light of given refrangibility incident on a given medium. Let some numerical quantity be taken for a measure of the refrangibility, suppose the refractive index in some standard substance. Let the refrangibilities of the incident and dispersed light be laid down along a straight line AX (fig. 2) taken for the axis of abscissæ; let AM represent the refrangibility of the incident light, and draw a curve of which the ordinates shall represent the intensities of the component parts of the truly dispersed beam. According to the law above stated, no part of the curve is ever found to the right of the point M; but in other respects its form admits of great latitude. Sometimes the curve progresses with tolerable uniformity, sometimes it presents several maxima and minima, or even appears to consist of distinct portions. Sometimes it is well separated from M, as in fig. 2; sometimes it approaches so near to M that the most refrangible portion of the truly dispersed beam is confounded with the beam due to false dispersion.

82. Let  $f(x)$  be the ordinate of the curve corresponding to the abscissa  $x$ ,  $a$  the abscissa of the point M. Since  $f(x)$  is equal to zero when  $x$  exceeds  $a$ , the curve must reach the axis at the point M at latest, unless we suppose the function capable of altering abruptly, as is represented in fig. 3. I do not think that such an abrupt alteration, properly understood, is necessarily in contradiction with the law of continuity. For the sake of illustration, let us consider the phenomenon of total internal reflexion. Let P be a point in air situated at the distance  $z$  from an infinite plane separating air from glass. Conceive light having an intensity equal to unity, and coming from an infinitely distant point, to be incident internally on this plane at an angle  $\gamma + \theta$ , where  $\gamma$  is the angle of total internal reflexion. The intensity at P is commonly, and for most purposes correctly, considered as altering abruptly with  $\theta$ , having, so long as  $\theta$  is negative, a finite value which does not vanish with  $\theta$ , but being equal to zero when  $\theta$  is positive. The mode in which the law of continuity is in this case obeyed is worthy of notice. In the analytical expression for the vibration, when  $\theta$  passes from negative to positive, the coordinate  $z$  passes from under a

circular function into an exponential with a negative index, containing in its denominator  $\lambda$ , the length of a wave of light. As  $\theta$  increases through zero, the expression for the vibration alters continuously; but if  $z$  be large compared with  $\lambda$  it decreases with extreme rapidity when  $\theta$  becomes positive. On account of the excessive smallness of  $\lambda$ , it is sufficient for most purposes to consider the intensity as a function of  $\theta$  which vanishes abruptly; and indeed it would be hardly correct to consider it otherwise. For the use of the term *intensity* implies that we are considering light as usual, whereas those phenomena which require us to take into account the disturbance in the second medium which exists when the angle of incidence exceeds that of total internal reflexion, lead us to consider the nature as well as the magnitude of that disturbance, which no longer consists of a series of plane waves constituting light as usual. It is in some similar sense that I mean to say that we may suppose the function  $f(x)$ , which expresses the intensity of the truly dispersed light, to alter abruptly, without thereby implying any violation in the law of continuity. In observing by the fourth method, the portion of the spectrum operated on, though it may be small, is necessarily finite, and in some cases no separation could be made out between the beams of truly and falsely dispersed light. Hence I cannot undertake to say from observation, whether the variation of  $f(x)$  be always continuous, though sometimes very rapid, or be in some cases actually abrupt. I think, however, that observation rather favours the former supposition, a supposition which, independently of observation, seems by far the more likely.

83. Although the law mentioned in Art. 80 is the only one which I have been able to discover, relating to the connexion between the intensity and the refrangibility of the component parts of the dispersed beam, which appears to be always obeyed, and which admits of mathematical expression, there are some other circumstances usually attending the phenomenon which deserve notice.

When dispersion commences almost abruptly on arriving at a certain point of the spectrum, the dispersed beam is very frequently almost homogeneous at first, and of the same refrangibility as the active light. If the dispersed beam, when first perceived, be decidedly heterogeneous, its refrangibility extends almost, if not quite, to that of the active light, so that it is difficult, if not impossible, to separate the beams of truly and falsely dispersed light. On the other hand, when dispersion comes on gradually, it is generally found that the refrangibility of even the most refrangible part of the dispersed beam does not come up to that of the active light.

Thus in the cases of the red dispersion exhibited by a solution of leaf-green, and of the orange dispersions exhibited by solutions obtained from archil and from the *Mercurialis perennis*, the dispersed light was at first nearly homogeneous, and of the same refrangibility as the active light. In the case of the green dispersions shown by a solution obtained from archil, and by canary glass, the dispersed light was heterogeneous from the first; but still, when it first commenced, a portion of it had nearly the same refrangibility as the active light. In a solution of sulphate of quinine

the dispersion came on gradually, being perceptible when the active light belonged to the middle of the spectrum; and in this case the dispersed light consisted of colours of low refrangibility. The bright part of the dispersion however came on pretty rapidly, when the active light approached the extreme limit of the visible spectrum, and accordingly the dispersed beam consisted in that case chiefly of light of high refrangibility.

84. The mode of absorption of any medium may very conveniently be represented by a curve, as has been done by Sir JOHN HERSCHEL. To represent geometrically in a similar manner the mode of internal dispersion, would require a curved surface. Let the refrangibility of light be measured as before, and suppose for simplicity's sake the intensity of the incident light to be independent of the refrangibility, so that  $dy$  may be taken to represent the quantity of incident light of which the refrangibility lies between  $y$  and  $y+dy$ . Considering the effect of this portion of the incident light by itself, let  $x$  be the refrangibility of any portion of the dispersed light, and  $zdx dy$  the quantity of dispersed light of which the refrangibility lies between  $x$  and  $x+dx$ . Then the curved surface, of which the coordinates are  $x, y, z$ , will represent the nature of the internal dispersion of the medium. We must suppose the intensity of the incident light referred to some standard independent of the eye, since the illuminating power of the rays beyond the violet, and even of the extreme violet, is utterly disproportionate to the effect which in these phenomena they produce.

From the nature of the case, the ordinate  $z$  of the surface can never be negative. The law mentioned in Art. 80 may be expressed by saying, that if we draw through the axis of  $z$  a plane bisecting the angle between the axes of  $x$  and  $y$ , at all points on the side of this plane towards  $x$  positive, the curved surface confounds itself with the plane of  $xy$ .

85. Let us consider the form of this surface in two or three instances of internal dispersion. For facility of explanation, suppose the plane of  $xy$  horizontal, let  $x$  be measured to the right,  $y$  forwards, and  $z$  upwards. Let a line drawn in the plane of  $xy$  through the origin, and bisecting the angle between the axes of  $x$  and  $y$ , be called for shortness the line  $L$ . In all cases the surface rises above the plane of  $xy$  only to the left of the line  $L$ .

In the case of a solution of leaf-green, the surface consists as it were of two mountain ranges running in a direction parallel to the axis of  $y$ , or nearly so. The first range, if prolonged, would meet the axis of  $x$  at a point corresponding to the place of the dark band No. 1 in the red, or nearly so. The second would meet it somewhere in the place corresponding to the green. The green range is much broader than the red, but very much lower, and is comparatively insignificant. The ridge of the red range is by no means uniform, but presents a succession of maxima and minima. The range commences at the end nearest to the axis of  $x$  with a very high peak, by far the highest in the whole surface. In following the ridge forwards,

five minima or passes may be observed, with hills intervening. The ordinates  $y$  of the first four of these minima correspond to the refrangibilities of the bright bands Nos. 2, 3, 4 and 5. The last minimum lies a little further on. Whether similar minima exist in the green range is not decided by observation, on account of the faintness of the green dispersed light.

In the case of canary glass, the surface consists of five portions like mountain ranges running parallel to the axis of  $y$ , and having abscissæ belonging to the red, reddish orange, yellowish green, green, and more refrangible green, respectively. These ranges do not all start from the immediate neighbourhood of the line  $L$ , but on the side towards the axis of  $x$  end almost in cliffs, at points at which the ordinate  $y$  is nearly equal to the abscissa of the fifth range, perhaps a little less. Thus the first three ranges are well separated from the line  $L$ . The ranges are intersected by a sort of valley running parallel to the axis of  $x$ , and having for its ordinate  $y$  the refrangibility of  $F\frac{1}{3}G$ . With the exception of the minima which occur where the ranges are intersected by this valley, the ridges run on very uniformly, and it is only very gradually that the ranges die away.

The form of the surface which expresses the internal dispersion of a solution of sulphate of quinine, may be gathered from the description of that medium. In this case the surface resembles a rising country, not intersected by any remarkable mountain ranges or valleys.

Fig. 4 is a rude representation of the internal dispersion in a solution of leaf-green. The curves represented in the figure must be supposed to be turned through  $90^\circ$  about the lines on which they stand, and will then represent sections of the surface already described, made by vertical planes parallel to the axis of  $x$ .  $OL$  is the straight line bisecting the angle  $xOy$ . The figure is merely intended to assist the reader in forming a clear conception of the general nature of the phenomena, and must not be trusted for details. No attempt is made to represent the several maxima and minima in the intensity of the red beam of dispersed light. In any such figure, if we suppose homogeneous light to be incident on the medium, and wish to lay down the place of the falsely dispersed beam, we have only to draw a straight line parallel to the axis of  $x$ , through the point in the axis of  $y$  which corresponds to the refrangibility of the incident light, and find where this line cuts the straight line  $OL$  which bisects the angle  $xOy$ .

*On the cause of the clearness of fluids, notwithstanding a copious internal dispersion which they may exhibit.*

86. It has been already remarked, that though water holding a water colour in suspension makes an admirable imitation of a highly sensitive fluid, when the latter is viewed by dispersive reflexion alone, the two fluids have a totally different appearance when viewed by transmitted light. The cause of this difference appears to be plain enough. The light due to internal dispersion emanates from each portion of



the fluid which is under the influence of the active light, and emanates apparently in all directions alike. I have not attempted to determine experimentally whether the intensity is strictly the same in all directions. The experiment would be very difficult, especially for directions nearly coinciding with that of the active light, because in that case the light which was really due to internal dispersion would be mixed up with the glare which is always found in the neighbourhood of light of dazzling brightness. However, I have seen nothing which led me to suppose that the intensity was different in different directions. We may express the results of observation extremely well, by saying that the fluid or solid medium is self-luminous so long as it is under the influence of the active light.

Accordingly, when a bright object, such as the sky, or the flame of a candle, is viewed through a highly sensitive fluid, the regularly transmitted light is accompanied by some side light due to internal dispersion. The latter, however, emanating in all directions alike from the influenced particles, is too faint, when contrasted with the regularly transmitted light, to make any sensible impression on the eye. But when a fluid, itself insensible, holds in suspension a great number of solid particles of finite size, the light reflected from such particles is reinforced, in directions nearly coinciding with that of the incident light, by a great quantity of diffracted light, so that a bright object viewed through such a fluid is surrounded by a sort of nebulous haze, giving the fluid a milky appearance.

#### *Washed Papers.*

87. In a paper "On the Action of the Rays of the Solar Spectrum on Vegetable Colours," Sir JOHN HERSCHEL mentions a peculiarity which he had observed in paper washed with tincture of turmeric, which consists in its being illuminated, when a pure spectrum is thrown on it, to a much greater distance at the violet end than is the case with mere white paper\*. This phenomenon was attributed by Sir JOHN to a peculiarity in its reflecting power, and was considered as a proof of the visibility of the ultra-violet rays. The colour of the prolongation of the spectrum was yellowish green. Sir JOHN appears to have been in doubt whether the greenish yellow colour was to be attributed to the mixture of the true colour of the ultra-violet rays with the yellow of the paper due to diffused light, or to the real colour of the ultra-violet rays themselves, which on that supposition would have been incorrectly termed "lavender."

88. The fact of the change of refrangibility of light having been established, there could be little doubt that the true cause of the extraordinary prolongation of the spectrum on paper washed with tincture of turmeric, was very different from what Sir JOHN HERSCHEL had supposed, and that it was due to a change of refrangibility in the incident light, which was produced by the medium in a solid state. Tincture of turmeric has already been mentioned as a medium which possesses in a high

\* Philosophical Transactions for 1842, p. 194.

degree the property of internal dispersion. It was the observation of Sir JOHN HERSCHEL's already mentioned, which led me to try this medium. But it is by no means essential that a sensitive substance should be in solution, or in the state of a transparent solid, in order that the change of refrangibility which it produces should admit of being established by direct experiment, although of course the mode of observation must be changed.

89. A piece of paper was prepared by pouring some tincture of turmeric on it, and allowing it to dry. In this way the part which was deeply coloured by turmeric was in juxtaposition with the part which remained white, which was convenient in contrasting the effects of the two portions. The sun's light being reflected horizontally into a darkened room through a vertical slit, the paper was placed in a pure spectrum formed in the usual manner. On the coloured part the fixed lines were seen with the utmost facility far beyond the line H, on a yellowish ground. The colours too of all the more highly refrangible part of the spectrum were totally changed. From the red end, as far as the line F, or thereabouts, there was no material change of colour; but a little further on a very perceptible reddish tinge came on, which was quite decided at  $F\frac{1}{2}G$ , where it was mixed with the proper colour of that part of the spectrum. About  $G\frac{4}{7}H$  the colour became yellowish. The reality of a change of refrangibility was easily proved by refracting the spectrum on the screen by a prism applied to the eye. When the refraction took place in a plane parallel to the fixed lines, they were seen distinctly throughout the spectrum; but when it took place in a plane perpendicular to the former, the fixed lines in the less refrangible part of the spectrum, and as far as F, were distinctly seen; but in the rest of the spectrum they were more or less confused, or even wholly obliterated, according to their original strength, the refracting angle and dispersive power of the prism, and its distance from the paper. With a prism of small angle the edges of the broad bands H were seen tinged with prismatic colours.

90. The change of refrangibility was further shown by the following observation. The paper was placed in the pure spectrum in such a manner that the line of junction of the coloured and uncoloured parts ran lengthways through the spectrum, so that the same fixed line was seen partly on the coloured and partly on the uncoloured portion. On viewing the whole through a prism of moderate angle applied to the eye, and so held as to refract the system in a direction perpendicular to the fixed lines, the line F was seen uninterrupted, but G was dislocated, the portion formed on the yellow part of the paper being a good deal less refracted than that formed on the white. The latter was indeed faintly prolonged into the yellow part of the paper, so that on this part G was seen double; but the image which was by far the more intense of the two was less refracted than that formed on the white paper. The whole appearance was such as to create a strong suspicion of some illusion, as if some other group of fixed lines formed on the yellow part of the paper had been mistaken for G, though certainly no reason appears why such a group should not have had its coun-

terpart on the white part. However, to remove all doubts, I refracted the system in the direction of the fixed lines, and then turned the prism round the axis of the eye through  $90^\circ$ , when the plane of refraction was situated as before. At first the two portions of the line G were of course seen in the same straight line; and the perfect continuity with which, as the prism turned round, the appearance changed into what had been first seen, left not the shadow of a doubt as to the reality of the dislocation.

91. The cause of the whole appearance is plain enough. The light coming from the illuminated part of the yellow paper consisted, in the neighbourhood of G, of two portions; the first, indigo light, which had been scattered in the ordinary way; the second and larger portion, heterogeneous light having a mean refrangibility a good deal less than that of G, which had arisen from homogeneous light of higher refrangibility. The absence of the first occasioned the faint prolongation of the more refracted part of the line G; the absence of the second gave rise to the less refracted part.

92. The broad bands H were seen faintly but quite distinctly on the white paper. On refracting them sideways by a prism of moderate angle held to the eye, they became confused, and tinged with prismatic colours. The confused images of these bands, seen in the white and coloured parts, were nearly continuous. It thus appears that the visibility of the bands H on the white paper was due to a change of refrangibility which that substance had produced in violet light of extreme refrangibility.

93. Effects similar to those produced by paper coloured by tincture of turmeric are also produced by turmeric powder, or even by the root merely broken across. Notwithstanding the roughness of the latter, the bands H and fixed lines far beyond are seen with the utmost facility.

94. These phenomena are much better observed by covering the slit with a deep blue glass, which absorbs all the bright part of the spectrum, while it freely transmits the violet and invisible rays, which are mainly efficient in this class of phenomena. In this way fixed lines may be seen on common white paper far beyond H. These lines may be seen without the use of the blue glass, by allowing the bright colours to pass by the edge of the paper, and receiving on it only the extreme violet and invisible rays.

95. Paper coloured by turmeric having exhibited so well the sensibility of that substance, I was induced to try various other washed papers, in fact, papers washed with most of the fluids with which I had made experiments. I found almost always that sensitive solutions gave rise to sensitive papers, exhibiting a change of refrangibility of the same character as that shown by the solution. Besides the turmeric paper, the two most remarkable were paper washed with a pretty strong solution of sulphate of quinine, and paper washed with the extract from the seeds of the *Datura stramonium*. I should here observe, that it was not till long after the time when these experiments were made that I was acquainted with the high sensibility of a decoction of the bark of the horse-chestnut. The former of the papers just mentioned ex-

hibited the fixed lines of the invisible rays on a blue, and the latter on a green ground. The dispersion produced by the quinine paper was not exhibited so early in the spectrum as in the case of turmeric, nor was it so copious in the extreme violet rays, and for some distance further on, but the quinine paper seemed superior to the other for showing the fixed lines of extreme refrangibility. With the turmeric paper the group  $n$  was plain enough, but with the quinine paper I have seen some fixed lines of the group  $p$ . The stramonium paper was, on the whole, I think superior to the quinine paper in point of the copiousness of the dispersed light, but seemed hardly equal to it for showing the fixed lines of extreme refrangibility. However, it is likely that paper washed with a solution of the sensitive principle in a state of purity would have been quite equal to the quinine paper in this respect.

96. A washed paper is a little more convenient for use than a solution, but, as might be expected, it does not show the fixed lines with quite as much delicacy, nor is it quite so good for tracing the spectrum to the utmost limits to which it can be traced with the substance employed.

97. The sensibility of fresh leaf-green could not be made out on a washed paper by this mode of observation, but the sensibility of the substance extracted by alcohol from black tea, from which the brown colouring matter had been removed by hot water, was plainly exhibited by the redness which it produced in the highly refrangible part of the spectrum.

98. Paper washed with a solution of guaiacum seemed an exception to the general rule; but this is not to be wondered at, since a paper prepared in this manner is turned green when exposed to the light, and it is difficult to prevent some degree of discoloration. That the fluid state is not essential to the exhibition of the sensibility of this substance, was however plainly shown by the high degree of sensibility of the solid resin from which the solution was made. In this case the bands H were seen on a greenish ground. The dispersion of a fine blue light under the influence of rays of still higher refrangibility was hardly, or not at all, exhibited by the solid resin.

99. Shell-lac, common resin, glue, are all highly sensitive. The ground on which the fixed lines in the neighbourhood of H are seen is brown in the case of shell-lac, and greenish in the case of resin and glue. The sensibility of glue is evidently not due to gelatine, for isinglass is almost, if not quite, insensible. These are merely a few instances of sensibility: I shall defer further mention of the subject till I have described a better mode of observation. I will merely observe for the present, that several washed papers proved not greatly inferior to turmeric paper for showing the fixed lines about and beyond H.

*Effect of refracting a Narrow Spectrum in a Vertical Plane.*

100. In the arrangement last described, when a short slit is used, the spectrum received on the washed paper or other substance is of course narrow, so that the fixed lines formed on the paper are but short, and may roughly be regarded as mere

points. If, now, the whole be viewed through a prism, so as to be refracted in a vertical plane, the effect is very striking. For facility of explanation suppose the red to be to the left, and the rays to be refracted upwards, so that to the observer the image is thrown downwards. The original spectrum on the screen is decomposed by the prism held to the eye into two spectra, which diverge from each other. The first of these runs obliquely downwards from left to right, and contains the natural colours of the spectrum from red to violet. It consists of light which has been scattered in the ordinary way by the substance on which the primary spectrum is received, and the cause of its obliquity is evident. The second spectrum is horizontal, that is to say, it approximates to the form of a long rectangle having its longer sides horizontal. Of course it would be theoretically possible to render the vertical sides the longer, but when the whole arrangement of the apparatus is such as to be convenient for observation, the horizontal sides are much longer than the others. In this second spectrum the colours run *horizontally*, that is to say, the lines of equal colour are horizontal. The interruptions of the primary spectrum corresponding to fixed lines, almost reduced to points, are now elongated, so that in this strangely formed spectrum the principal fixed lines of the solar spectrum are seen running *across* the colours.

101. It will be convenient to have a name for the second of the two spectra above mentioned. As the term *secondary spectrum* is already appropriated to something altogether different, I shall call it the *derived spectrum*. The first of the diverging spectra may be called the *primitive spectrum*, while the original spectrum, considered as not yet decomposed by the prism held to the eye, may be called, for distinction, as in fact it has been already called, *primary*.

102. In accordance with the law enunciated in Art. 80, it is found that the derived spectrum appears *always on one and the same side* of the primitive, being *less refracted*.

103. The brilliancy of the derived spectrum, its extent, both vertically and horizontally, the colours of which it mainly consists, the distribution of its illumination in a horizontal direction, all depend upon the nature of the substance upon which the primary spectrum is received. As a general rule, it may be stated that it starts from the neighbourhood of the brightest part of the primitive spectrum, and extends from thence onwards to a good distance beyond the extreme violet; and that with a given substance its colour is pretty uniform, that is, does not much change in passing from one vertical section to another. Sometimes the derived spectrum remains very bright up to its junction with the primitive, or at least till it gets so near that the superior brilliancy of the primitive spectrum prevents all observation on the derived; sometimes it remains dull to a considerable distance from the primitive spectrum, and then, opposite a highly refrangible part of the primitive spectrum, a strong illumination comes on in the derived, lasts for some distance, and afterwards gradually dies away. Many of the results mentioned in this paragraph are better observed by a somewhat different method, which will shortly be described.

104. It has been already stated that the bands H were distinctly seen on common white paper, the substance usually employed as a screen in experiments on the spectrum, but that this was due to a change of refrangibility produced in the extreme violet rays. These same bands have been seen on paper in the experiments of others, though of course their visibility was not attributed to its true cause. By the method of observation described in Art. 100, or still better, by a method not yet explained, it may be seen that the change of refrangibility produced by white paper is by no means confined to the extreme violet rays, and those still more refrangible, but extends from about the middle of the spectrum to a good distance beyond the extreme violet. The distance to which the illumination can be traced by means of light merely scattered in the ordinary way, may be seen by examining the primitive spectrum. In the primitive spectrum formed on white paper and other white substances, I have not been able to trace the illumination beyond the edge of the broad band H, which accords very well with the illuminating power of the extreme violet when received directly into the eye.

*Illuminating Power of the Rays of high Refrangibility.*

105. The prolongation of the spectrum seen on turmeric paper was brought forward by Sir JOHN HERSCHEL as a proof of the visibility of the ultra-violet rays, or rather as a confirmation of other experiments which had led him to the same conclusion. Of course, the experiment with turmeric must now be regarded as having no bearing on the question; but from the way in which Sir JOHN speaks of it, it would appear that he thought the other experiments not so conclusive as to be independent of the confirmation which they received from this. The experiment with the distorted spectrum, indeed, must now be put out of account, because in this experiment, as I have been informed by Sir JOHN HERSCHEL, the light was only thrown on a screen. Accordingly, the question of the visibility of these rays may be regarded as open to further investigation.

While engaged in some of the experiments described in Art. 89, I had occasion to form a pure spectrum in air in a well-darkened room, the slit itself by which the sun's rays entered being covered by a deep blue glass, so that no great quantity of light entered even at this quarter. Now, if ever, it would appear that the ultra-violet rays ought to be seen by receiving them directly into the eye; for the blue glass was so transparent with regard to these rays that the fixed lines far beyond H were seen with facility, even on substances, such as white paper, which stand low in the scale of sensibility; and the length of the spectrum from B to H was about an inch and a quarter, so that when the extreme violet rays entered the pupil, supposed to be held near the pure spectrum, not only the extreme red rays transmitted by the blue glass, but even the brighter part of the transmitted blue and violet rays fell altogether outside it. However, on holding the eye a few inches in front of the pure spectrum, so as to see the fixed lines distinctly, the bands H were indeed seen with

great facility; but I was not able to make out fixed lines beyond the end of the group *I*, that is, about the end of FRAUNHOFER's map. However, the eyes of different individuals may differ much in their power of being affected by the highly refrangible rays. It must be confessed, that on looking in the direction of the prisms, a good deal of blue light was seen, consisting of light which had been scattered at the surfaces of the prisms and lens. This light, though far from dazzling, was sufficient to prevent the eye from seeing excessively faint objects, even though they might be well defined. For want of a heliostat, I did not attempt an experiment I was meditating for securing a more perfect isolation of the ultra-violet rays\*.

However, it seems to me to be a point of small importance, so far as regards its bearing on other physical questions, whether the illuminating power of these rays is absolutely null or only excessively feeble. It is quite certain, that if not absolutely null, their illuminating power is at least utterly disproportionate to the effect which they produce in the phenomena to which the present paper relates, and indeed that is true even of the violet rays. By *illuminating power*, I mean of course, power of producing the sensation of light when received directly into the eye; for by giving rise to light of lower refrangibility, they are able to illuminate strongly an object on which they fall.

*Mode of Observation specially applicable to Opaque Bodies.*

106. In some of the experiments already described, the change of refrangibility was exhibited, which was produced by washed papers and solid bodies. There exists, however, a mode of observation far preferable to those which have already been explained as applicable to such cases, and which may even in some instances be employed with advantage in the examination of transparent bodies. In the experiment described in Art. 100, the primitive spectrum is pure, but the derived spectrum impure, on account of the finite length of the slit. Were the slit reduced to a point, it is true that the derived spectrum would become pure like the primitive, but then the quantity of light would be so small that the primary spectrum would hardly bear prismatic analysis. It is well, once for all, to examine a few sensitive opaque substances in a very pure spectrum, because then the exhibition of fixed lines running across the colours in the derived spectrum removes even the shadow of a doubt as to the reality of the change of refrangibility of the incident light. Besides this, the only theoretical advantage in having the primitive spectrum very pure is, that it might be expected to enable us to detect any very rapid fluctuations in the colour or intensity of the dispersed light. Of course, I am now speaking only with reference to experiments in which the observer is employing the spectrum to examine some substance, not employing the substance to examine the spectrum. But practically, I have not found any advantage on this account; for abrupt, or almost abrupt changes in the colour or intensity of the dispersed light hardly ever, if ever, occur,

\* See note B.

except when the active and the dispersed light have very nearly the same refrangibility. But such changes could not be observed even with a pure primitive spectrum, because in the place where they occur the primitive and derived spectra overlap; and independently of this, the brilliancy of the primitive spectrum would prevent all exact observation of the derived. It is true, that in the case of chlorophyll, or some of its modifications, changes of intensity having apparently somewhat the same nature were observed when the active and the dispersed light were widely separated in refrangibility. But the sensibility of this substance is difficult, if not impossible, to observe in the case of a washed paper or a green leaf, except by one of the methods not yet described, so that it is not to be expected that such fluctuations could be made out. Besides, it is to be remembered that the fluctuations observed in the case of solutions of chlorophyll, were fluctuations in the rate at which dispersed light was produced, not fluctuations in the sum total of the dispersed light produced by the time the active light was exhausted. Fluctuations of the former kind by no means imply fluctuations of the latter; and indeed, the circumstance, that maxima of activity in the solution correspond to minima of transparency, would seem to show that the total quantity of light dispersed, considered as a function of the refrangibility of the active light, is not subject to these fluctuations, or at least not to anything like the same extent. Now the total quantity of red light dispersed by a green leaf, or by a paper washed with a solution of chlorophyll, must depend upon the sensibility of this substance and upon its transparency conjointly, and therefore it is likely enough that such maxima and minima would not be observed, even were the dispersed light much stronger than it is.

107. Suppose now the slit by which the light enters to be placed in a horizontal instead of a vertical position, so as to lie in the plane of refraction. Corresponding to light of any given refrangibility, the image of the slit formed after refraction through the prisms and lens will now be a narrow parallelogram, which may be regarded as a horizontal line. The series of these lines, succeeding one another in a horizontal direction, and consequently overlapping, forms the spectrum incident on the body examined. This spectrum is now no longer pure, but only approximately so, a point, however, which, as we have seen, is not of much consequence. But by this trifling sacrifice two very great advantages are gained. The first is increase of illumination. When the slit is vertical, the spectrum received on the body occupies a rectangle having for breadth the length of the image of the slit; but when it is horizontal, the same, or very nearly the same quantity of light is concentrated into a rectangle having the same length as before (the length of the image of the slit being disregarded compared with that of the spectrum), but having for its breadth only the length of the image of a line drawn across the slit. Hence the intensity of the incident light is increased in the ratio of the breadth to the length of the slit. The second advantage is purity in the derived spectrum, a point of much consequence, because sometimes the composition of this spectrum presents very remarkable



peculiarities. If the slit be not too long, the spectrum formed in air is still sufficiently pure to allow us to make out in a general way what are the refractivities of those portions of the incident light which are most efficient in producing dispersed light; and this is nearly all that can be done even when the spectrum is very pure.

108. The method of observation which has just been described is that which latterly I have almost exclusively employed in examining opaque substances. As it will be convenient to have a name for it, I shall speak of examining a substance in a *linear spectrum*. In examining substances which are only slightly sensitive, it is often highly advantageous to cover the slit with a blue glass.

109. Fig. 5 is intended to represent the usual appearance of the primary linear spectrum, and of the primitive and derived spectra. XY is the primary spectrum, as seen by the naked eye, RV, ST are the primitive and derived spectra into which it is separated by the prism held to the eye. The direction of the shading in RV is intended to represent the composition of this spectrum, which may be regarded as consisting of an infinite number of images of the slit arranged obliquely in the order of their refractivity. The direction of the shading in ST is that of the lines of the same colour and same refractivity. Of course the figure does not represent the amount of vertical displacement of the primary spectrum when viewed through the prism held to the eye.

110. There is another mode of observation which I have occasionally found convenient when the object was to determine whether a substance exhibited so much as a low degree of sensibility. In this method the sun's light was reflected horizontally through a large lens, and then transmitted through a small lens placed in the condensed beam. The small lens was covered by a small vessel with parallel sides of glass, containing a blue ammoniacal solution of copper, or else by a deep blue glass combined with a weak solution of nitrate or sulphate of copper. The object of the latter solution was to absorb the extreme red which is transmitted by a blue glass. The light coming through the lens was then analysed by a prism, being received directly into the eye, or else allowed to fall on a white object which had been previously ascertained not to change the refractivity of the light incident upon it. I found clean white earthenware to serve very well for such an object, but each observer ought to test for himself the substance he employs. When a test object, such as white earthenware, is used, it is placed at the focus of the lens, and the spot of blue light formed upon it is analysed by a prism to see if the absorption is sufficient. When the visible rays are considered to have been sufficiently absorbed, the object to be observed is placed at the focus of the lens, and the spot of light formed upon it is viewed through a prism. The spectrum then seen is compared with that given by the test object. This method of observation is rather easier than that of a linear spectrum, and is at least as delicate if the object be merely to determine whether a substance is sensitive or not, but on the whole it is not near so useful. It may sometimes be used with advantage in the case of translucent bodies.

111. An extremely pale solution of nitrate or sulphate of copper is sufficient to absorb the extreme red transmitted by a deep blue glass. This is not the case with the ammoniacal solution, which does not absorb the extreme red till it is of a pretty deep blue. Its absorbing power is greatest, not at the extreme red, but about the orange, as may be seen by using candle-light, which is richer in red rays than daylight.

112. Another method of observation which is sometimes useful, consists in employing a large lens and absorbing medium, as described in Art. 110, but leaving out the additional small lens. The substance to be examined is placed in the condensed beam, and viewed through an absorbing medium which is approximately complementary to the former. This method is chiefly useful in examining a confused mass of various substances. The most minute fragments of sensitive substances show themselves in this manner.

*Results obtained with a Linear Spectrum.*

113. When this method is applied to the examination of common objects, it is found that the property of producing a change of refrangibility in the incident light is extremely common. Thus, wood of various kinds, cork, horn, bone, ivory, white shells, leather, quills, white feathers, white bristles, the skin of the hand, the nails, are all more or less sensitive. To make a list of sensitive substances would be endless work; for it is very rare to meet with a white or light-coloured organic substance which is not more or less sensitive. I am not now speaking of organic substances obtained in a state of chemical isolation, of which some are sensitive and others insensible. That substances of a dark colour should frequently prove insensible is only what might have been expected, because the dispersed light is not reflected from the surface, but emanates from all points of a stratum of finite thickness; and in order that dispersed light should be forthcoming, it is necessary that the active light entering, and the dispersed light of a different refrangibility returning, should both escape absorption on the part of the colouring matter. Such substances usually consist of a mixture of various chemical ingredients, of which one or more may very likely be sensitive, in which case the substance may be compared to a solution of sulphate of quinine mixed with ink. Frequently however the colouring matter is itself sensitive.

114. Among sensitive substances I have mentioned the skin of the hand, which stands rather low in the scale. I have found the back of the hand a convenient test object. When the sunlight is not strong enough to show with ease the derived spectrum in the case of the hand, there is little use in attempting to observe.

115. It is needless to say that papers washed with tincture of turmeric, or with a solution of sulphate of quinine, display their sensibility in a remarkable manner when examined in a linear spectrum. The sensibility of turmeric paper is rather impaired by exposing the paper to the light, but on the other hand is materially increased by washing it with a solution of tartaric acid.

116. Paper washed with an ethereal solution from dried archil exhibited very well the sensibility of that substance. The derived spectrum consisted chiefly of two distinct portions, one containing orange and a little red, the other consisting chiefly of green, just as in the beam of dispersed light, produced by white light taken as a whole, which the solution itself exhibited. Indeed, I have found that the prismatic composition of dispersed light could be determined even more conveniently by means of a linear spectrum than by means of the beam dispersed by a solution.

117. The inside of the capsules of the *Datura stramonium* is nearly white, and apparently uniform. But when the capsules are examined in a linear spectrum, certain patches shine out like bright clouds in the invisible rays. The whole of the inside is sensitive, as such substances almost always are, but these patches, which are probably spots against which the seeds have pressed, are remarkably so. The capsules were examined after they had begun to burst.

118. By means of a linear spectrum the sensibility of chlorophyll may be detected in a green leaf. It is exhibited by the appearance in the derived spectrum of a narrow pure red band of remarkably low refrangibility. The refrangibility is so low that I have always found this band separated from the derived spectrum due to other sensitive substances with which chlorophyll or one of its modifications might have been mixed.

119. The petals of flowers, so far as I have examined, are as a class rather remarkable for their insensibility, some appearing quite insensible, and others only slightly sensitive. The bright yellow chaffy involucre of a species of everlasting, proved, however, highly sensitive, and its sensibility was also displayed in an alcoholic solution. This medium was sensitive enough to exhibit a pretty copious dispersive reflexion of a pale greenish yellow light. Its sensibility was more confined than usual to the rays of very high refrangibility.

120. Among petals, the most remarkable which I have observed are those of the purple groundsel (*Senecio elegans*). These petals disperse a red light, more copious than is usual among petals. If a petal be placed behind a slit, and the transmitted light be analysed, it is found to exhibit three remarkable bands of absorption, much resembling those of blue glass, but closer together, and beginning later in the spectrum, the first appearing about the place of the orange. These bands are still better seen in a solution of the colouring matter in weak alcohol. On examining this medium by the third method, with a lens of shorter focus than usual, and looking down from above, the places of the absorption bands were indicated by tooth-shaped interruptions in the beam of light reflected from motes. The points of these teeth were occupied by red dispersed light, which did not appear in the intervening beams of light reflected from motes, from whence it appears that there is the same sort of connexion between the absorption and dispersion of this medium as was noticed in Art. 59, in the case of solutions of chlorophyll and its modifications.

121. A collection of sea-weeds appeared all more or less sensitive, most of them highly so. All, or almost all, except the white ones, exhibited in the derived spectrum the peculiar red band indicative of chlorophyll and its modifications. The transmitted light also exhibited more or less the absorption bands due to this substance, which was likewise, in the specimens tried, extracted by alcohol. But the most remarkable example of sensibility found in sea-weeds occurs in the case of the red colouring matter contained in orangy red, red, pink, and purple sea-weeds. To judge by its optical properties, this colouring matter appears to be the same in all cases, but to be mixed in different proportions with chlorophyll, or some modification of it, and probably other colouring matters, thus giving rise to the various tints seen in such sea-weeds. The derived spectrum exhibited by sea-weeds of this kind consists mainly of a band of unusual brightness, containing some red, followed by orange and yellow. This band fades away gradually at its less refrangible limit, where it is separated by a dark interval from the narrow well-defined red band of still lower refrangibility due to chlorophyll. At its more refrangible limit, however, it breaks off with unusual abruptness.

122. When the light transmitted through such a sea-weed is subjected to prismatic analysis, in addition to one at least of the absorption bands due to chlorophyll, there is seen a band obliterating the yellow, another dividing the green from the blue, and a third, far less conspicuous, dividing the green into two. The whole of the green is absorbed more rapidly than the blue beyond, and not merely than the red, which last is the final tint.

123. The red colouring matter is easily extracted by cold water from certain kinds of red sea-weed, if fresh gathered; but when once the plant has been dried, the colouring matter cannot be extracted in any way that I know of. It is apparently insoluble in alcohol and ether, and is decomposed by boiling. Cold water extracts only a trace of it after a long time.

124. A piece of recently gathered red sea-weed, on being mashed with cold water, readily gave out its red colouring matter. When the residue was treated with alcohol, the fluid was almost immediately coloured green by chlorophyll, whereas this substance is only very slowly and sparingly extracted by alcohol from dried sea-weeds. A dried sea-weed may apparently be assimilated to an intimate mixture of gum and resin, which it would be very difficult to dissolve, whether it were attacked by water or alcohol.

125. The solution of the red colouring matter was highly sensitive, exhibiting a copious dispersive reflexion of a yellowish orange light. The transmitted light was pink or red, according to the thickness through which the light passed. When this light was analysed, the same three absorption bands which have been already mentioned were perceived. The analysis of the light transmitted by the fronds of various red sea-weeds had rendered it extremely probable that the faint division in the

green did belong to the red colouring matter; but till I had obtained this matter in solution I did not feel certain that it might not have been due to chlorophyll, the spectrum of which exhibits a division in the green.

126. When this fluid was examined in Sir DAVID BREWSTER's manner, and the dispersed beam was analysed, the spectrum was found to consist of a broad band like that which has been already described as seen in the derived spectrum given by a frond of red sea-weed. When the solution, which happened to be very weak, was examined by the third method, the dispersion was found to be produced chiefly by a portion of the incident spectrum, having a breadth about equal to that of the interval between the two principal bands of absorption. To each of these bands corresponded a maximum of activity. The tint of the dispersed light was nearly uniform; but by the fourth method of observation some faint dispersed red could be made out, which appeared before the main part of the dispersion had come on. This medium affords a very good example of an intimate connexion between absorption and internal dispersion.

127. The colouring matters of birds' feathers appeared to be insensible, white feathers being most sensitive, pale ones next, and dark ones not at all: however, I have not examined a large collection.

128. Of coloured fruits, such as currants, &c., the colouring matter appeared, in the very few cases which I have examined, to be quite insensible.

129. A set of water colours were by no means remarkable for sensibility, but rather the contrary. The inorganic colours appeared quite insensible, except white lead, the sensibility of which was perhaps due to size, and offered nothing striking, either as to its character or as to its amount. Some lakes and other organic colours proved moderately sensitive. But I found one water colour, called Indian yellow, which stands pretty high among sensitive substances. In its mode of dispersion it much resembles turmeric, but it does not come up to that substance in the amount of sensibility. It is said to be composed of urate of lime, but I do not know how far it may be regarded as chemically pure.

130. Many of the substances used in dyeing, and dyed articles in common use, furnish very remarkable examples of sensibility. Archil, litmus and turmeric have been already mentioned; and I have been recently informed by a friend that the *Mercurialis perennis*, in which a striking instance of sensibility was observed, was formerly employed in dyeing. A piece of scarlet cloth, examined in a linear spectrum, gave a copious derived spectrum which was very narrow, consisting chiefly of the more refrangible red. With a vertical slit the bands H and fixed lines beyond were seen on a red ground. Paper washed with a solution of cochineal and afterwards with a solution of alum, when examined in a linear spectrum, displayed a pretty high degree of sensibility, the derived spectrum consisting in this case of a red band. If tartaric acid be used instead of alum, the dispersion is a good deal more copious.

Common red tape is another example in which the derived spectrum is very copious,

consisting mainly of a red band. Some red wool, dyed I suppose with madder, proved extremely sensitive. The derived spectrum in this case was pretty broad, but red was the predominant colour. Green wool, dyed I do not know with what, was also very sensitive, giving a pretty broad derived spectrum, in which green was the predominant colour. These examples may suffice, but the reader must not suppose that they form the only instances in which dispersion was observed among dyed substances. On the contrary, it is extremely common in this class.

131. Brazil wood, safflower, red sandal wood, fustic and madder, all gave rise to solutions having a pretty high degree of sensibility. The solutions here referred to were such as were obtained directly by water, &c., in which the colours which these substances are capable of producing were not brought out. The beautiful red colouring matters of logwood and camwood appear to be insensible; for a fresh-made solution of logwood in water exhibited no perceptible sensibility, and the slight sensibility exhibited by a similar solution of camwood seemed to have no relation to the red colouring matter.

132. Paper washed with a solution of madder in alcohol was sensitive in a pretty high degree, but the sensibility was greatly increased by afterwards washing with a solution of alum. Accordingly I found that a decoction of madder in a solution of alum exhibited a very high degree of sensibility, displaying a copious dispersive reflexion of a yellow light. In this medium the dispersion commenced about the fixed line D, and continued from thence onwards far beyond the extreme violet, so that the group of fixed lines  $n$  was seen with great ease.

133. Safflower red, examined in the shape in which it is sold on what is called a *pink saucer*, proved highly sensitive, giving a bright and narrow derived spectrum, which consisted chiefly of the more refrangible red. This substance possesses some other remarkable optical properties, which however do not belong to the immediate subject of this paper.

134. Metals proved totally insensible. I have examined gold, platinum, silver, mercury, copper, iron, lead, zinc and tin. Brass is like simple metals in this respect; but if the surface be lackered the lacker displays its own sensibility.

135. The non-metallic elements, carbon, sulphur, iodine and bromine, are insensible.

136. Among common stones I have found dark flint, limestone, chalk and some others which were sensitive, though only in a low degree compared with organic substances. To guard against any impurity of the surface, the stones were broken across, and the fresh surface examined. In the cases mentioned, the sensibility observed is not to be attributed to the chief ingredient of the stone, for quartz, chalcedony, Iceland spar and Carrara marble were insensible.

*Compounds of Uranium.*

137. Towards the end of last autumn, when the lateness of the season afforded but few opportunities for observation, I learned from different sources that the kind of yellow glass which has been already mentioned as possessing in so high a degree the property of internal dispersion was coloured with oxide of uranium. This rendered it interesting to examine other compounds of uranium; and I accordingly procured some crystallized nitrate of the peroxide, which, with a few other compounds formed from it, and some of the natural minerals which contain uranium, were examined by methods which have been already explained.

138. The crystals of the nitrate were not sufficiently large and perfect to admit of observation by the methods applicable to fluids and clear solids, but they could be readily observed by means of a linear spectrum. They proved to be sensitive in a very high degree, dispersing a green light which had the same very remarkable composition that has been already described in the case of the yellow glass. On placing a crystal in the continuation of the same linear spectrum with the glass, and viewing the whole through a prism, the five bright bands of which the derived spectrum given by each of the two media usually consisted, appeared to correspond to one another as regards their position in the spectrum. With great concentration of light I have seen an additional band of greater refrangibility in the spectrum of the crystals.

139. Some crystals of nitrate of uranium were gently heated so as to expel a good part at least of the water of crystallization. The residue after some time became opaque and nearly white. In this state it was still more sensitive than the crystals. The dispersed light was not exactly of the same tint, but more nearly white; and the derived spectrum was found on being analysed to contain, in addition to the bright bands usually seen in the derived spectrum of the crystals, another blue band still more refrangible. The fused mass gradually attracted moisture from the air, its colour changed to that of the crystals, and the most refrangible of the bright bands disappeared from the derived spectrum. Although when the incident light was very much concentrated I have seen this band even in the crystals, it was faint compared with the preceding bands, whereas in the case of the whitish mass its intensity was not very different from that of the others. It appears therefore that the quality as well as the quantity of the dispersed light was altered by depriving the crystals of a part of their water.

140. A solution of nitrate of uranium in water is decidedly sensitive, though not sufficiently so to exhibit much dispersive reflexion. When the dispersed beam is analysed it is resolved into bright bands. When the solution is examined in a pure spectrum, the mode of dispersion is found to agree with that of canary glass. The dispersion commences abruptly at the same part of the spectrum as in the case of the glass, and after a rather narrow band in which light is copiously dispersed, there follows a remarkable minimum of sensibility, just as in the glass (see Art. 76.), where the dispersed light is almost imperceptible. After this the dispersion is resumed,

and offers nothing remarkable. The minimum of sensibility occurs at the very same place in the spectrum, whether the sensitive medium be a solution of nitrate of uranium or glass coloured yellow by uranium.

141. *Yellow Uranite*.—This mineral, when examined in a linear spectrum, proved to be sensitive in an extremely high degree. The derived spectrum consisted, as in the case of the glass, of bright bands arranged at regular intervals, but in this case six were seen, a band being visible in the faint red at the extremity of the spectrum which could not be made out in the case of the glass.

142. *Green Uranite, or Chalcolite*.—According to M. PELIGOT the formula of the yellow uranite of Autun is  $\text{PhO}^5$ ,  $\text{CaO}$ ,  $2(\text{U}^2\text{O}^2\text{O})$ ,  $8\text{HO}$ , and the green uranite differs from the yellow only in having the lime replaced by oxide of copper\*. Yet a specimen of green uranite on being examined in a linear spectrum proved totally insensible. The primitive spectrum showed however a very remarkable system of dark bands depending on the absorption of light by the mineral. In examining these bands, the previous prismatic decomposition of the light, so far from being necessary, is decidedly inconvenient. It is better to dispense with the prisms altogether, using only the lens, and placing the mineral so that the image of the slit is formed upon it. The bright line thus formed is viewed from a convenient distance through a prism, the eye being held out of the direction of regular reflexion. The position of any bands which may appear in the spectrum can then be determined by means of the fixed lines, which are seen at the same time; or, if it be desired to see the latter more distinctly, it will be sufficient to attach a fragment of paper to the mineral or other substance, placing it so that the image of the slit is formed partly on the paper and partly on the substance to be examined. I have frequently found this mode of observation convenient in examining the absorption of light by opaque substances. The manner in which the absorption of the medium comes into play in this case will be considered in greater detail further on (see Art. 176.).

143. When green uranite was examined in this manner, it showed a very remarkable system of dark bands of absorption. These bands were seven in number, or at any rate six, and were arranged with all the regularity of bands of interference. The first was situated at about  $b\frac{4}{7}\text{F}$ , the second at  $\text{F}$ ; the middle of the sixth fell a very little short of  $\text{G}$ ; the third, fourth and fifth were arranged at regular intervals between the second and sixth; the seventh was situated about as far beyond the sixth as the sixth beyond the fifth. The spectrum was so faint in the region of the seventh band as to leave some slight doubts respecting its existence. There would not have been light enough to see bands further on.

144. Uranite is highly lamellar in its structure, from whence it is otherwise called uran-mica. The reader may perhaps suppose that the dark bands described in the last paragraph were bands of interference, which I had mistaken for bands of absorption, and that they were really of the nature of NEWTON'S rings, or more exactly of

\* Annales de Chimie, tom. v. (1842) p. 46.



the bands seen in an experiment due to the Baron von WREDE. There may, it will perhaps be said, have been a fissure parallel to the first surface, so as to separate a thin plate; and the interference of the two streams of light reflected respectively on the upper and under surface of this plate may have produced the bands observed. But various phenomena attending these bands are irreconcilable with such a supposition. Towards the edges of the crystal, where flaws did in fact exist, bands of the same nature as Von WREDE's were actually observed. But these had an appearance totally different from that of the others. The dark bands of the interference system were more intensely black and better defined than those of the other system, and were very variable, depending as they did upon the thickness of the plate by which they were formed, whereas the bands belonging to the first system were always the same. Besides, were these bands due to interference, there is no reason why they should be confined to one region of the spectrum, and that by no means the brightest. However, to take away all possible doubts respecting the nature of the bands, I detached a small scale from the crystal, and having placed it behind a slit in a beam of sunlight condensed by a lens, I analysed the transmitted light by a prism. Were the bands really due to absorption, they ought to be more distinct in the transmitted light, whereas, were they of the nature of Von WREDE's bands, they ought to be faint, and almost imperceptible. The spectrum of the transmitted light contained however four dark bands, which were well defined and intensely black. The whole of the spectrum beyond the place of the next band was absorbed, which is the reason why four bands only were visible.

145. The absorption bands of green uranite, though they showed great regularity with respect to their positions, did not appear very regular with regard to their intensities. The second, fifth and sixth seemed to me to be more conspicuous than the first, third and fourth. I cannot say for certain whether this ought to be attributed to fluctuations in the absorbing power of the medium, or fluctuations in the original intensity of the solar spectrum, but I am strongly inclined to prefer the former view.

146. The intervals between the absorption bands of green uranite were nearly equal to the intervals between the bright bands of which the derived spectrum consisted in the case of yellow uranite. After having seen both systems, I could not fail to be impressed with the conviction of a most intimate connexion between the causes of the two phenomena, unconnected as at first sight they might appear. The more I examined the compounds of uranium, the more this conviction was strengthened in my mind.

147. Yellow uranite exhibits a system of absorption bands similar to those of green uranite. Nitrate of uranium also shows a similar system. In a solution I have observed seven of these bands arranged at regular intervals. The first absorption band coincided with F, the fifth with G nearly. The absorption bands may also be seen by analysing the light transmitted through the crystals. The following arrangement exhibited at one view the absorption bands and those due to the light which had changed its refrangibility.

148. The sun's light was reflected horizontally by a mirror, and condensed by passing through a large lens. It was then transmitted through a vessel with parallel sides containing a moderately strong ammoniacal solution of a salt of copper. The strength of the solution, and the length of the path of the light within it, were such as to allow of the transmission of a little green besides the blue and violet. A crystal of nitrate of uranium was then attached to a narrow slit, and placed in the blue beam which had been transmitted through the solution, the crystal being turned towards the incident light. The light coming from the crystal through the slit was then viewed from behind, and analysed by a prism. A most remarkable spectrum was thus exhibited, consisting from end to end of nothing but bands arranged at regular intervals. The interval between consecutive bands appeared to increase gradually from the red to the violet, just as is the case with bands of interference. Although this interval appeared to alter continuously from one end of the spectrum to the other, the entire system of bands was made up of two distinct systems, different in appearance, and very different in nature. The less refrangible part of the spectrum, where only for the crystal there would have been nothing but darkness, was filled with narrow bright bands, due to the light which had changed its refrangibility. These bands were much narrower than the dark intervals between them, but they were not mere lines containing light of definite refrangibility. The more refrangible part of the spectrum was occupied by the system of bands of absorption. The interval between the most refrangible bright band and the least refrangible dark band of absorption appeared to be a very little greater than one band-interval, so that had there been one band more of either kind the least refrangible absorption band would have been situated immediately above the most refrangible bright band. With strong light I think I have seen an additional band of this nature.

149. *Pitchblende*.—This mineral proved to be quite insensible, and exhibited nothing remarkable.

150. *Hydrate of Peroxide of Uranium*.—Some crystallized nitrate of uranium was exposed to a heat a good deal short of redness, whereby most of the acid was expelled. The residue was of a deep brick-red colour, and consisted no doubt chiefly of anhydrous peroxide. It was quite insensible. In order to remove any undecomposed nitrate, it was boiled with water, whereby the undecomposed nitrate was dissolved, and the peroxide converted into a hydrate. This hydrate, after having been washed and dried at the temperature of the air, was of an extremely beautiful yellow colour, and was I suppose the hydrate  $U^2O^3 + 2HO$  described in chemical treatises. It was tolerably sensitive, in fact for an inorganic substance extremely so, though the sensibility was much less than that of nitrate of uranium, yellow uranite, or canary glass. The derived spectrum consisted as before of separate bright bands. A small portion of the powder was attached by water to blotting-paper, and dried before a fire. The powder thus obtained on paper was duller than before, and inclined a little more to orange, though the colour was not much deeper than that of the former hydrate.

From its colour and the circumstances of its formation, it was probably the other hydrate  $U^2O^3 + HO$ . It proved on examination to be totally insensible.

151. *Acetate of Peroxide of Uranium*, prepared by dissolving the yellow hydrate of the peroxide in acetic acid, and evaporating to crystallize.—This salt is extremely sensitive, about as much so as the nitrate. The derived spectrum consisted of six bright bands arranged at regular intervals. It seemed to me that the last five of these were respectively a little more refrangible than the five bands given by the nitrate, and then a sixth band was visible in the faint red in the case of the acetate which was not ordinarily seen in the nitrate. However, this observation has need to be repeated under more favourable circumstances.

152. Nitrate and acetate of peroxide of uranium, yellow uranite, and canary glass, are all so highly sensitive as to allow the primary spectrum to be examined with a prism at some distance. In the first three media the bright bands are narrow, much narrower than the dark intervals between; in the glass they appear much broader than in the other media.

153. *Oxalate of Peroxide of Uranium*, prepared in the manner mentioned by M. PELIGOT, namely, by adding a saturated solution of oxalic acid to a solution of nitrate of uranium, washing and drying the precipitate.—This salt was sensitive, but only in a low degree. However, the derived spectrum bore prismatic examination sufficiently to show three or four bright bands. The absorption of the medium was examined by spreading some of the powder on glass along with water and allowing it to dry. The layer was then examined by different methods. The salt exhibits three very intense absorption bands in the highly refrangible part of the spectrum. The positions of these bands, by measurement, were F 0.31 G, F 0.58 G, F 0.85 G.

154. *Phosphate of Peroxide of Uranium*, prepared by precipitation from a solution of nitrate of uranium by adding a solution of common phosphate of soda.—This salt was sensitive, though not in a high degree. It was a good deal more sensitive than the oxalate, but I think not so much so as the hydrate of the peroxide. The derived spectrum consisted of bright bands as usual\*.

155. *Uranate of Potassa*, prepared by dropping a solution of nitrate of uranium into a solution of caustic potash, stopping long before the alkali was neutralized.—This salt was found to be insensible, both in its original state as a gelatinous hydrate, and in various stages of drying.

156. *Uranate of Lime*, prepared in a similar manner with lime-water.—This salt, which after drying is of a fine orange colour, was like the preceding found to be insensible. It seemed interesting to examine these two salts, because the former contains two elements (not counting oxygen) in common with canary glass, and the latter two elements in common with yellow uranite. Yet the salts are insensible while the two other media are so remarkably sensitive.

157. *Solutions by means of alkaline carbonates*.—It is known to chemists that alka-

\* See note C.

line carbonates, added in solution to a solution of nitrate of uranium, give yellow precipitates which are redissolved in an excess of the precipitant. The solutions thus obtained with the carbonates of potassa and soda, which were of a greenish yellow colour, were found to be totally insensible. They exhibited however four of those singular absorption bands so characteristic of salts of peroxide of uranium. Of these the third fell a little short of G, its more refrangible edge nearly coinciding with that fixed line; the first and second were situated between F and G, the distance of the first beyond F being somewhat greater than the interval between two consecutive bands. The fourth, which was situated beyond G, was fainter than the others. The second and third were the most conspicuous of the set.

158. The absorption bands due to peroxide of uranium afford an easy mode of detecting that substance in solution. For this purpose the solutions mentioned in the preceding paragraph are much preferable to the nitrate, for they produce much stronger bands when only a small quantity of uranium is present. The absorption bands of nitrate of uranium are visible, as might have been expected, in presence of a large quantity of nitrate of copper\*.

#### *Optical Tests of Uranium in Blowpipe Experiments.*

159. When a bead of microcosmic salt is fused with oxide of uranium, and brought to its highest state of oxidation, it is yellow by transmitted light. Such a bead is sensitive in a very high degree, quite as much so as canary glass. When the light falls sideways on it, and it is held against black cloth or a dark object, it exhibits plainly the green colour due to internal dispersion. When properly examined by means of sunlight its sensibility is evident at once, and when the dispersed light is viewed through a prism it is resolved into bright bands. One of the most convenient modes of examining such minute objects consists in reflecting the sun's light horizontally through a large lens, intercepting by means of absorbing media all the rays except those of very high refrangibility, placing the object to be examined in the condensed beam, and viewing it through a prism. So delicate is this test when applied to uranium, that on one occasion, when engaged in examining a bead coloured green by chromium, which had been fused in the exterior flame, I observed the appearance given by uranium. This turned out to be actually due to uranium, of which a mere trace was accidentally present without my knowledge.

160. The green communicated to microcosmic salt by uranium after exposure to the reducing flame has a very peculiar composition, by means of which the presence of uranium may be instantly detected. For this purpose it is sufficient to view through a prism the inverted image of the flame of a candle formed by the bead, the latter being so held as to be seen projected on a dark object. The observation is perfectly simple, and occupies only a few seconds. The spectrum exhibits an isolated band at the red extremity, followed by a very intense dark band of absorption. A

\* See note D.

similar dark band, but not quite so intense, occurs in the green: beyond the green there is usually but little light seen. As the absorption progresses the first dark band invades all the space from the red to the green, and the spectrum consists of an isolated red band and a green band divided into two. In its mode of absorption, the medium has a strong general resemblance to chlorophyll. The green due to copper or to chromium shows nothing remarkable when viewed through a prism, and could not possibly be confounded with the green due to protoxide of uranium. The absorption bands due to this oxide are not completely brought out till the bead is cold.

161. Uranium produces the same effects with borax as with microcosmic salt, but they are less distinct, or at least less easily produced.

162. When the uranium contained in a bead of microcosmic salt is thoroughly oxidized, and the bead is gently heated, so as just to be self-luminous, the light which it gives out is not red, like that of most substances at a low heat, but green, or rather greenish white.

163. Solutions of protoxide of uranium have a very remarkable effect on the spectrum, resembling more or less that of a bead of microcosmic salt coloured green by uranium. Of course the absorption can be observed much better by means of a solution than by a mere bead. I have observed several bands of absorption in such solutions, but the cases which I have hitherto examined are too few to justify me in entering into detail. Besides, the absorption bands due to protoxide of uranium do not belong properly to my subject, the compounds of this oxide, so far as I have examined, being insensible.

*Appearance of highly Sensitive Media in a Beam from which the Visible Rays are nearly excluded.*

164. When a large beam of sunlight is reflected horizontally into a darkened room, and transmitted through an absorbing medium, placed in the window, of such a nature as to let pass only the feebly illuminating rays of high refrangibility and the invisible rays beyond, various sensitive media have a very strange and unnatural appearance when placed in the beam, on account of the peculiar softness of the dispersed light with which the media appear as it were self-luminous, and the almost entire absence of strong light reflected from convexities. Among substances eminently proper for this experiment, may be mentioned a solution of the bark of the horse-chestnut, or of sulphate of quinine, or of stramonium seeds, a decoction of madder in a solution of alum, and above all, ornamental articles of canary glass. The appearance of a specimen of yellow uranite was curiously altered by this mode of examination. By daylight the mineral appeared much of the same colour as the stone in which it was imbedded, but when placed in a beam such as that above mentioned the uranite was strongly luminous, while the stone remained dark.

*Natural Crystals.*

165. Of natural crystals I have hitherto examined only a small number. For a long time I was occupied almost exclusively with vegetable products, the mineral kingdom not appearing promising. However, I have found internal dispersion in certain specimens of apatite, arragonite, chrysoberyl, cyanite, and topaz. In all these cases the dispersion appeared due, as in the case of fluor-spar, to some substance accidentally present in small quantity; so that yellow uranite is at present the only natural crystal to the essential constituents of which the property of internal dispersion has been found to belong.

166. Among the minerals just mentioned apatite was the most sensitive, though it fell very far short of yellow uranite. That the sensibility was not due to phosphate of lime, was plain from the circumstances that a colourless specimen was insensible, and that the amount of sensibility was found to be different in different parts of the same sensitive specimen. With the exception of the colourless crystal already mentioned, all the specimens of apatite examined were of a greenish colour, and all were sensitive. The dispersed light was something of an orange colour, but was not homogeneous orange. In one specimen it consisted of three distinct bright bands at regular intervals. The mode in which the sensibility of this crystal was connected with the refrangibility of the incident rays was very peculiar. In arragonite dispersion was found in the transparent specimens examined; the translucent specimens were found to be insensible. The dispersed light was of a brownish white colour. In the same crystal some parts were insensible and others more or less sensitive. The portions of equal sensibility were arranged in plane strata, just as in the case of fluor-spar, as has been noticed by Sir DAVID BREWSTER. In a specimen which had been cut for showing conical refraction, the strata were in some places perpendicular to the plane of the optic axes, and in other parts parallel to the line bisecting the axes, and inclined to their plane at such an angle that the two directions of the strata must have been parallel to two of the commonest lateral faces. Another specimen showed strata parallel to an oblique terminal face. The strata are plainly due, as Sir DAVID BREWSTER has remarked with reference to fluor-spar, to some substance taken up during crystallization. Accordingly, they preserve a sort of history of the growth of the crystal. In a twin crystal of fluor-spar, the direction of the strata in that part of the mass which was common to the geometrical forms of both crystals, showed to which crystal it really belonged. In fluor-spar the strata are parallel to the faces of the cube, at least in the specimens which I have examined, and the same has been observed by Sir DAVID BREWSTER.

In chrysoberyl, cyanite and topaz, the dispersed light was red or reddish, and was too variable to allow of its being attributed to the essential constituents of the crystals. In these cases the sensibility was but slight; indeed in cyanite there was only a trace of dispersion when the crystal was examined under great concentration of light.

*Coloured Glasses.*

167. Besides canary glass, I have examined the common coloured glasses, including that coloured by gold, but with one exception have not met with any example in which the sensibility observed appeared to have any connexion with the colouring matter. The paler glasses exhibited a little internal dispersion, because the colour was not sufficiently intense to mask the dispersion which a common colourless glass would exhibit.

168. The exception occurred in the case of the pale brown glass, which has been already mentioned in connexion with my first experiment. This glass dispersed a red light under the influence of the highly refrangible rays. The colour of the light was not pure prismatic red, but red was predominant. A similar dispersion, due apparently to the same cause, was observed in the case of one of the common reddish brown German wine bottles. The sensibility of these glasses appears to be due to an alkaline sulphuret. A bead purposely coloured in this manner was in fact found to disperse a red light like the glasses. Moreover, in the confused masses obtained by fusing sulphate of soda and sulphate of potash on charcoal before the blowpipe, certain portions were found which dispersed a red light, and that pretty copiously for an inorganic substance. A similar dispersion was observed among the products obtained by fusing together sulphur and carbonate of potash, while other parts of the confused mass exhibited dispersion of a different kind. It seems plain that among the combinations of sulphur with the alkalies sensitive compounds exist, but what they are I have not examined.

*Cautions with respect to the discrimination between true and false internal dispersion.*

169. In the early part of this paper certain tests were given for distinguishing between true and false internal dispersion in a fluid. But it requires some experience in observations of this kind to be able readily to decide, and a too rigid adherence to one of the tests to the exclusion of the others might lead to error.

The first test relates to the continuous appearance of a truly dispersed beam. But sometimes solid particles exist in mechanical suspension, which are so fine and so numerous, that this test alone might lead the observer to mistake a falsely for a truly dispersed beam. On the other hand, if a fluid which itself alone exhibits no internal dispersion, true or false, hold solid particles in what is obviously mere mechanical suspension, we must not immediately conclude that the medium, taken as a whole, is incapable of changing the refrangibility of any portion of the light incident upon it. For we have seen that the fluid state is not in the least degree essential to the exhibition of sensibility, and of course a fluid will serve as well as anything else for the mere mechanical support of a sensitive substance.

170. Thus lycopodium is very sensitive, as appears by examining the powder in a linear spectrum. Accordingly, I found that when a little lycopodium was mixed with water, and the whole medium was examined by the fourth method, it displayed

its sensibility, although the beam of light which had changed its refrangibility was plainly discontinuous. When Indian yellow was used instead of lycopodium, the whole medium exhibited its sensibility when it was examined by the fourth method. In this case the suspended particles were so fine that the beam of light which had changed its refrangibility appeared to be continuous, though of course it was not really so. In observing with muddy fluids like these, it is almost necessary to employ absorbing media, since otherwise the effect of the light scattered at the surfaces of the prisms and large lens might lead the observer to conclusions altogether erroneous.

171. The next test relates to the polarization of a falsely dispersed beam. Being engaged on one occasion in examining the effects of acids and alkalies on a weak solution of a sensitive substance, employing sunlight which had been merely reflected through a small lens, I met with a beam which had every appearance of having been only falsely dispersed, but on viewing it from above through a doubly refracting prism I was surprised at first by finding it unpolarized. It soon occurred to me that the beam must have been due, not to solid motes, but to excessively small bubbles of carbonic acid gas, the existence of which was thus revealed, though they were too small to be seen directly. The light being incident on these bubbles at an angle of about  $45^\circ$ , which is very little less than the angle of total reflexion, the reflected light would be almost perfectly unpolarized\*.

172. Water which had been merely boiled in a test tube gave a similar result. The unpolarized beam of falsely dispersed light was of course due in this case to the air which had been held in solution. This shows why long-continued boiling should be necessary, in order to free water from air. It is not that the affinity of water for air is so great as to be only gradually overcome, but that the air, immediately expelled from solution when the temperature rises sufficiently, is still retained in a state of mechanical mixture, forming excessively minute bubbles, the terminal velocity of which is insensible. Accordingly it is not till larger bubbles are formed, by the casual meeting of a number of these small bubbles, that the air rises to the surface and escapes.

173. With respect to the test of true dispersion depending on the change of refrangibility, it has been already remarked that in some cases the change is so slight, that if this test alone were applied, the observer might mistake true dispersion for false. However, it is only in rare cases that there is any danger of being deceived in this manner in the application of the test; but on the other hand, in observing a muddy fluid or a translucent solid by the fourth method, the observer, if not on his guard, might easily be deceived by the effect of scattered light, and be led to mistake false dispersion for true. Thus suppose the medium to be water holding in suspension particles of an insensible water colour, and the small lens to be placed a little beyond the commencement of the violet. Two beams of light would enter the lens, namely, a regularly refracted beam of violet, and a scattered beam of white light.

\* See note E.



Of these the latter would be insignificant compared with the former, were it not that the illuminating power of the colours belonging to the middle of the spectrum is so very much greater than that of the violet. When the dispersed beam was analysed by a prism, it would be decomposed into a violet beam of definite refrangibility, followed by a dark interval, and then a broad band containing the colours of the brighter part of the spectrum in their natural order. This is what is constantly seen in cases of true dispersion; but the polarization of the beam, and its behaviour under the action of absorbing media, would reveal the counterfeit character of the dispersion.

*On the Colours of Natural Bodies.*

174. By this expression I mean to include only the colours to which it is usually applied, namely, those of leaves, flowers, paints, dyed articles, &c., which form the great mass of the colours that fall under our observation. I do not refer to colours due to refraction, such as those of the rainbow, or to diffraction, such as those of the coronæ seen about the sun and moon, or to interference, such as those seen in the clear wings of small flies, or to the colours which accompany specular reflexion, which last are usually but slight, though sometimes pretty intense.

In some few instances, as for example in the case of fluor-spar, various salts of peroxide of uranium, acid solutions of disulphate of quinine, &c., colours are observed, sufficiently strong to arrest attention, which have a remarkable and hitherto unsuspected origin. But I am not now speaking of colours arising from a change of refrangibility in the incident light. In the vast majority of cases these colours are far too feeble to form any sensible portion of the whole colour observed. The colours which dyed articles give out under the influence of the highly refrangible rays usually agree more or less nearly with those of which such substances commonly appear, and it is possible that the colour arising from a change of refrangibility may contribute in some slight degree to the brilliancy of the tint observed. If, however, the effect be sensible I am persuaded that it is but slight; and very brilliant colours may be produced without a change of refrangibility, as for example in the case of biniodide of mercury. For the present I shall neglect the light which may have changed its refrangibility.

175. Few, I suppose, now attach much importance to the bold speculations in which NEWTON attributed the colours of natural bodies to the reflexion of light from thin plates. Sir DAVID BREWSTER has shown how extremely different the prismatic composition of the green of the vegetable world is, from what it ought to be, according to NEWTON's theory, and what NEWTON supposed that it was. It is now admitted that the various colours of natural bodies are merely particular instances of one general phenomenon, namely, that of absorption. Absorption is most conveniently studied in a clear fluid or solid, but it does not the less exist in a body of irregular structure, such as a dyed cloth or a coloured powder.

The green colouring matter of leaves affords an excellent example of the identity of the effect produced on light by natural bodies and of ordinary absorption; for the same very peculiar system of absorption bands which are displayed by a clear solution of the colouring matter may be observed directly in the leaf itself. However, it is needless to bring forward arguments to support a theory now I suppose universally admitted; my present object is merely to point out the mode in which the colours which bodies reflect, or more properly scatter externally, depends upon the absorbing power of the colouring matter, so as to justify the conclusions deduced in Art. 142, from observations made in the manner there described.

176. Let white light be incident on a body having an irregular internal structure, such as a coloured powder. A portion will be reflected at the first irregular surface, but the larger portion will partly enter the particles, partly pass between them, and so proceed. In its progress the light is continually reflected in an irregular manner at the surfaces of the particles, and a portion of it is continually absorbed in its passage through them. For simplicity's sake, suppose the light incident in a direction perpendicular to the general surface, and neglect all light which is more than once reflected. Let  $t$  be the thickness of a stratum which the light has penetrated,  $I$  the intensity of the light at that depth, or rather the intensity of a given kind of light, so that the whole intensity may be represented by  $\int I d\mu$ ,  $\mu$  being the refractive index in some standard substance. In passing across the stratum whose thickness is  $dt$ , suppose the fraction  $qdt$  of the light to be absorbed, and the fraction  $rdt$  to be reflected and scattered in all directions, then

$$dI = -(q+r)Idt.$$

Integrating this equation, and supposing  $I_0$  to be the initial value of  $I$ , when  $t=0$ , we have

$$I = I_0 e^{-(q+r)t}. \quad \dots \dots \dots (a.)$$

For the sake of simplicity, suppose the body viewed in a direction nearly perpendicular to the general surface; and of the light reflected and scattered in passing across the stratum whose thickness is  $dt$ , suppose that the fraction  $n$  would enter the eye if none were lost by absorption, &c. Then the intensity of the light coming from that stratum would be  $nrIdt$ . But in getting back across the stratum whose thickness is  $t$ , the intensity is diminished in the ratio of  $I_0$  to  $I$ . Hence if  $I'$  be the intensity of the light actually entering the eye,

$$dI' = nrI_0^{-1} I^2 dt = nrI_0 e^{-2(q+r)t} dt.$$

If we suppose the thickness of the body sufficient to develop all the colour which the body is capable of giving, the superior limit of  $t$  will be  $\infty$ , and we shall have

$$I' = \frac{nr}{2(q+r)} I_0. \quad \dots \dots \dots (b.)$$

177. The colour which accompanies ordinary reflexion being usually but slight, I shall neglect the chromatic variations of  $r$ . It is  $q$  which is subject to extensive and apparently capricious variations, depending upon the refrangibility of the light.

Imagine two curves drawn whose abscissæ are proportional to  $\mu$ , and ordinates proportional to the ratio of  $I$  to  $I_0$  for the first, and the ratio of  $I'$  to  $I_0$  for the second. These curves will serve to represent to the mind the composition of the light transmitted through a stratum of the body having a thickness  $t$ , and of that reflected from the body when seen in mass. It is plain that the maximum and minimum ordinates in the two curves will correspond to the same abscissæ; but unless  $t$  be very small, so small as to be insufficient to bring out the colour of the medium seen by transmission, the maxima and minima will be much more developed in the first curve, whose ordinates vary as  $e^{-qt}$ , than in the second, whose ordinates vary as  $(q+r)^{-1}$ . If, then, the absorbing power be subject to fluctuations depending on the refrangibility of the light, the bands of absorption may be observed either in the reflected or in the transmitted light, but they admit of being better brought out in the latter.

178. If the nature of the substance be given,  $q$  will be given. If now the body be of a loose nature, as for example blue glass reduced to a fine powder,  $r$  will be considerable. Hence, in accordance with the expression (b.), the quantity of light scattered externally will be considerable, but the tint will be but slight. If the powder be now wetted, the reflexions at the surfaces of the particles will be diminished,  $r$  will be diminished, and, as appears from (b.), the quantity of light scattered externally will be diminished, but at the same time the tint will be deepened, since the chromatic variations of  $I'$  are increased. If the body be compact and nearly homogeneous,  $r$  will be small, and therefore very little light will be returned, except what is regularly reflected at the first surface. The tint of the small quantity of light which is reflected otherwise than regularly, will be somewhat purer than before, inasmuch as the chromatic variations of  $I'$  tend to become the same as those of  $q^{-1}$ .

*On the nature of False Dispersion, and on some applications of it.*

179. It has been already stated that a beam of falsely dispersed light seen in a fluid has generally more or less of a sparkling appearance, indicating that it owes its origin merely to motes held in mechanical suspension. Sometimes, however, no defect of continuity is apparent. This is especially the case when two fluids are mixed together, of which one contains in solution a very small quantity of a substance which we might expect to be precipitated by the addition of the other, or when a slightly viscous fluid has remained quiet for a long time. If some part at least of a falsely dispersed beam be plainly due to motes, that does not of course prove for certain that there is no part which may have a different origin, and may be essentially connected with true dispersion; nor do the theoretical views which I entertain of the cause of the latter lead me to regard it as at all impossible that a beam polarized in the plane of reflexion, and having the same refrangibility as the incident light, may be a necessary accompaniment of true dispersion. However, observation, I think, points in a contrary direction; for although more or less of

false dispersion is almost always exhibited along with true dispersion, the quantity of the former seems to have no relation to the quantity of the latter, but does seem to have relation to the greater or less degree of clearness which we should be disposed to attribute to the fluid.

180. The phenomenon of false internal dispersion seems to admit of being applied as a chemical test to determine whether or not precipitation takes place. Thus, if a little tincture of turmeric be greatly diluted with alcohol, and then water be added, a yellow fluid is obtained which appears to be perfectly clear, exhibiting no sensible opalescence; but the occurrence of a copious false dispersion when the fluid is examined by sunlight, reveals at once the existence of suspended particles, though they are too minute to be seen individually, or even to give a discontinuous appearance to the falsely dispersed beam. Although such a precipitation could not, I suppose, be used as a means of mechanical separation, it might still be useful as pointing out the possibility of an actual separation under different circumstances as to strength of solution, &c.

181. One of the best instances of false dispersion that I have met with, best, that is, in forming a most excellent imitation of true dispersion, occurred in the case of a specimen of plate-glass which was made, as I was informed, with a quantity of alkali barely sufficient. This glass, which was very slightly yellowish brown, when viewed edgewise by transmitted light, had a bluish appearance when viewed properly, strongly resembling that of a decoction of the bark of the horse-chestnut, diluted with water till the dispersed light is no longer concentrated in the neighbourhood of the surface. But when the glass was examined by sunlight, the polarization of the dispersed beam, and the identity of its refrangibility with that of the incident light, showed that this was merely an instance of false dispersion. Another very good example of false dispersion is afforded by chloride of tin dissolved in a very large quantity of common water.

182. When a horizontal beam of falsely dispersed light is viewed from above, in a vertical direction, and analysed, it is found to consist chiefly of light polarized in the plane of reflexion. It has often struck me, while engaged in these observations, that when the beam had a continuous appearance, the polarization was more nearly perfect than when it was sparkling, so as to force on the mind the conviction that it arose merely from motes. Indeed, in the former case, the polarization has often appeared perfect, or all but perfect. It is possible that this may in some measure have been due to the circumstance, that when a given quantity of light is diminished in a given ratio, the illumination is perceived with more difficulty when the light is uniformly diffused than when it is spread over the same space, but collected into specks. Be this as it may, there was at least no tendency observed towards polarization in a plane perpendicular to the plane of reflexion, when the suspended particles became finer, and therefore the beam more nearly continuous.

183. Now this result appears to me to have no remote bearing on the question of

the direction of the vibrations in polarized light. So long as the suspended particles are large compared with the waves of light, reflexion takes place as it would from a portion of the surface of a large solid immersed in the fluid, and no conclusion can be drawn either way. But if the diameters of the particles be small compared with the length of a wave of light, it seems plain that the vibrations in a reflected ray cannot be perpendicular to the vibrations in the incident ray. Let us suppose for the present, that in the case of the beams actually observed, the suspended particles were small compared with the length of a wave of light. Observation showed that the reflected ray was polarized. Now all the appearances presented by a plane-polarized ray are symmetrical with respect to the plane of polarization. Hence we have two directions to choose between for the direction of the vibrations in the reflected ray, namely, that of the incident ray, and a direction perpendicular to both the incident and the reflected rays. The former would be necessarily perpendicular to the directions of vibration in the incident ray, and therefore we are obliged to choose the latter, and consequently to suppose that the vibrations of plane-polarized light are perpendicular to the plane of polarization, since experiment shows that the plane of polarization of the reflected ray is the plane of reflexion. According to this theory, if we resolve the vibrations in the incident ray horizontally and vertically, the resolved parts will correspond to the two rays, polarized respectively in and perpendicularly to the plane of reflexion, into which the incident ray may be conceived to be divided, and of these the former alone is capable of furnishing a reflected ray, that is of course a ray reflected vertically upwards. And in fact observation shows, that, in order to quench the dispersed beam, it is sufficient, instead of analysing the reflected light, to polarize the incident light in a plane perpendicular to the plane of reflexion.

Now in the case of several of the beams actually observed, it is probable that many of the particles were really small compared with the length of a wave of light. At any rate they can hardly fail to have been small enough to produce a tendency in the polarization towards what it would become in the limit. But no tendency whatsoever was observed towards polarization in a plane perpendicular to the plane of reflexion. On the contrary, there did appear to be a tendency towards a more complete polarization in the plane of reflexion.

M. BABINET has been led by the same reasoning to an opposite conclusion respecting the direction of the vibrations in polarized light, resting on an experiment of M. ARAGO's, in which it appeared that when light was incident perpendicularly on the surface of white paper, and the reflected or rather scattered light was viewed in a direction almost grazing the surface, it was found to be partially polarized in the plane of the sheet of paper\*. But the actions which take place when light is incident on a broad irregular surface, like that of paper, bounding too a body which is so translucent that a great part of the light must enter it and come out again, appear

\* Comptes Rendus, tom. xxix. p. 514.

to me to be too complex to allow us to deduce any conclusion from the result respecting the direction of vibration. Besides, the result itself admits of easy explanation, by attributing it to the light which has entered the substance of the paper and come out again, which might be expected to be polarized by refraction.

*Effect of Heat on the Sensibility of Glass, &c.*

184. The sensibility of glass is temporarily destroyed by heat. The glass may be heated by holding it in the flame of a spirit-lamp, as a heat much short of redness is sufficient. This takes place even with glass coloured by oxide of uranium, which is in general so highly sensitive. The sensibility returns again as the glass cools. A bead of microcosmic salt, containing uranium in its highest state of oxidation, is very sensitive when cold, but insensible when hot. The sensibility gradually comes on as the bead cools. A solution of nitrate of uranium in water on being heated has its sensibility impaired, very much so by the time the temperature reaches the boiling-point. The sensitive compounds, whatever may have been their precise nature, obtained by fusing the sulphates of soda and potassa on charcoal before the blow-pipe, were insensible while hot. The few vegetable solutions which I have examined with this object did not seem to have their sensibility affected by being heated.

*Effect of Concentration and Dilution.*

185. In investigating the change of refrangibility produced by a sensitive substance in solution, it is almost always convenient to have the solution weak. This however is by no means merely a matter of convenience, for the quantity of light which the medium is capable of giving back with a changed refrangibility is often materially diminished by increasing the concentration of the solution. Thus a solution which, when in a concentrated state, exhibits no sensible dispersive reflexion, will often exhibit when much diluted a very copious appearance of that nature. On the other hand, the dilution may of course be carried too far, so as to render imperceptible the peculiar properties of the substance dissolved. Yet it is wonderful what a degree of dilution a highly sensitive solution will bear before its sensibility ceases to be perceptible.

That the sensibility will be diminished, and will at last become imperceptible, if only the dilution be carried far enough, is nothing more than might have been predicted with the utmost confidence. In such a case the light passes completely through the fluid long before it has produced all the effect which it is capable of producing. But that concentration should be an obstacle to the exhibition of the phenomenon is not perhaps what we should have expected, and deserves an attentive consideration.

186. Imagine a given sensitive substance to be held in solution, in a vessel of which the face towards the eye is plane, and the breadth in the direction of vision as great as we please; and suppose the solvent, or at least the fluid used for diluting the solu-

tion, to be itself colourless and insensible. Suppose the fluid to be illuminated by light of given intensity and given refrangibility entering at the face next the eye, and let the eye E from a given position look in the direction of a given point P in the nearer surface of the vessel. In short, let everything be given except the strength of the solution. For the sake of simplicity regard the eye as a point, and make E the vertex of an indefinitely thin conical surface surrounding the line EP. Call this conical surface C, and let  $c$  be the surface within the fluid generated by right lines coinciding with the refracted rays which would be produced by incident rays coinciding with the generating lines of the surface C. This latter surface we may if we please regard as cylindrical, since we shall only be concerned with so much of the fluid contained within it as lies at a distance from P less than that at which the light entering the eye in consequence of internal dispersion ceases to be sensible; and in the cases to which the present investigation is meant to apply this distance is but small compared with PE. Let the fluid within  $c$  be divided into elementary portions by planes parallel to the surface of the fluid at P, and at distances from P proportional to the strength of the solution. It is evident that an element of a given rank, reckoned from P, will contain a constant number of sensitive molecules, and the incident light in reaching this element has to pass through a thickness of the medium such that a plate of the same thickness, and having a given area, contains a given number of sensitive or absorbing molecules. The same is true of the dispersed light which proceeds from the element and enters the eye. Now it seems natural to suppose that if the strength of a solution be doubled, trebled, &c., or reduced to one-half, one-third, &c., the quantity of light absorbed will be the same provided the length of the path of the light be reduced to one-half, one-third, &c., or doubled, trebled, &c. This comes to the same thing as supposing that each absorbing molecule stops the same fractional part of the light passing it, whether the solution be more or less dilute. We should similarly be inclined to suppose that each sensitive molecule would give out the same quantity of light, when influenced by light of given intensity, whether it belonged to a stronger or a weaker solution. If we admit these suppositions, it is plain that the quantity of dispersed light which reaches the eye from the element under consideration will be independent of the strength of the solution. This being true for each element in particular will be true for the aggregate effect of them all, and therefore the quantity of light exhibited by dispersive reflexion will be independent of the strength of the solution. It may be readily seen that the result will be the same if we take into account the finite size of the pupil.

187. Now this is by no means true in experiment. On examining in a pure spectrum a highly concentrated solution of sulphate of quinine, a copious dispersion was observed to commence a little below the fixed line G. It remained very strong as far as H, and beyond. In the weak solution first mentioned in this paper, it will be remembered that the dispersion seemed to come on about  $G\frac{1}{2}H$ . The reason of this, or at least one reason, is evident, and was very prettily shown by the form of the

space to which the dispersed light was confined. On looking down from above, so that this space was seen in projection, it appeared in the case of the weak solution to have approximately the form of the space contained between one branch of a rectangular hyperbola, one asymptote, and a line parallel to the other, the first asymptote being the projection of the anterior surface, and the line parallel to the other being the course of the least refrangible of the active rays which were capable of producing a sensible quantity of dispersed light. The breadth of the illuminated space, which among the most highly refrangible rays was almost insensible, continually increased, until the space ended in a blue beam which went quite across the vessel. But in the case of the strong solution the illuminated space had throughout an almost insensible breadth, except just close to its lower limit, that is, the limit corresponding to the least refrangible of the active rays, where it ended in a sort of tail or plano-concave wedge, which penetrated to a moderate distance into the fluid. Hence one reason, though perhaps not the only reason, why the strong solution showed a copious dispersion from  $G$  to  $G\frac{1}{2}H$ , where the weak solution showed hardly any, is plain enough. But in the region of the invisible rays beyond the violet, the dispersion was plainly more copious with the weak than with the strong solution. It appears then that in such a case the sensitive molecules do not act independently of each other, but the quantity of light emitted by a given number of molecules is less, in proportion to the light (visible or invisible) consumed, than when a solution is more dilute. We should expect *à priori* that when a solution is tolerably dilute further dilution would make no more difference in this respect. This seems to agree very well with experiment. For when a pretty dilute solution and one much more dilute are compared with respect to the quantity of dispersed light given out in a given portion of the incident spectrum, they appear to be alike. I suppose the comparison to be made with respect to such a portion of the incident spectrum, or in the case of solutions of such strength, that the dispersed light is confined to a space extending to no great distance into the fluid in either solution. Under these circumstances the comparison may be made easily enough.

188. In the actual experiment, the elementary portions of light coming from the elementary strata of fluid situated at different distances from the anterior surface enter the eye together. Let us however trace the consequences of the very natural supposition, that in passing across a given stratum of fluid the quantity of light absorbed, as well as the quantity given out by dispersion, is proportional, *cæteris paribus*, to the intensity of the incident light. The incident light is here supposed to be homogeneous, and to belong indifferently to the visible or invisible part of the spectrum. In crossing the elementary stratum having a thickness  $dt$ , let the fraction  $qdt$  of the incident light be absorbed, and the fraction  $r dt$  dispersed in such a direction as to reach the eye; and of the latter portion let the fraction  $s dt$  be absorbed in crossing a stratum having a thickness  $dt$ ,  $s$  being different from  $q$  on account of the change of refrangibility. Then by a very simple calculation similar to



that of Art. 176, we find for the intensity  $I'$  of the dispersed light which enters the eye

$$I' = \frac{r}{q+s} I_0,$$

$I_0$  being the intensity of the incident light. Since a sensitive fluid is in general coloured, and the dispersed light is in general heterogeneous,  $s$  will in general be different for the different portions into which the dispersed light would be decomposed by a prism. However, if the fluid be colourless, or all but colourless, as is the case with a solution of sulphate of quinine,  $s$  will be insensible, so that  $I'$  will be proportional simply to  $rq^{-1}$ . Hence from the observed variations in  $I'$ , arising from variations in the strength of the solution, we may infer the corresponding variations in  $rq^{-1}$ .

If, then, we represent by the ordinate of a curve the ratio of the quantity of light given out to the quantity of light absorbed by a given number of active molecules, the abscissa being the ratio of the quantity of diluting fluid to the quantity of the sensitive substance in solution, it appears that the curve will be concave towards the axis of the abscissæ, and will have an asymptote parallel to that axis.

#### *On the Choice of a Screen.*

189. We have seen that white paper, the substance commonly employed as a screen on which to receive the spectrum, gives back with a changed refrangibility a portion of the light incident upon it. This might in some cases lead an observer not aware of the circumstance to erroneous conclusions. Since the colour of dispersed light depends upon its refrangibility, which is different from that of the active light, the colours of a spectrum received on white paper must be somewhat modified. In truth the intensity of the light dispersed is so small compared with the intensity of the light scattered, that the modification is quite insensible except in the extreme violet. But beyond the extreme violet the spectrum seems to be prolonged with a sort of greenish gray tint, which belongs neither to that nor to any other part of the true spectrum. In experiments on absorption, if instead of receiving the light directly into the eye it be found convenient to form a pure spectrum on a screen of white paper, then, if the absorbing medium be placed in the path of the incident light, the scattered light forming any part of the spectrum cannot be cut off or weakened without at the same time cutting off or weakening the dispersed light coming from the same part of the screen. But if the absorbing medium be held in front of the eye, its effect on the spectrum will sometimes be very sensibly different from what it would be were the screen to send back none but scattered light.

It is true that the quantity of light dispersed by white paper is so small that this substance may very well continue to be used as a screen, without any danger of the observer's being deceived, if only he be aware of the fact of dispersion, so as to be on his guard. Still, it is not unreasonable to seek for a substitute for paper, which may be free from the same objection.

190. A porcelain tablet appeared to be unexceptionable in this respect, for it exhi-

bited no perceptible sensibility, even when examined by a linear spectrum. However, the translucency of the substance gave the spectrum a blurred appearance, and the fixed lines were not shown so well as on paper.

Chalk scraped smooth is well adapted, from its fineness, its whiteness and its opacity, for showing the most delicate objects. The finest fixed lines are beautifully seen on it, decidedly better than on paper. Its sensibility too, though not absolutely null, is much less than that of most kinds of white paper. Indeed, it would be an unnecessary refinement to seek for anything better, were it not that a piece of sufficient size might not always be at hand. From what I have seen, I believe that the best kind of screen will be obtained by the use of some white inorganic chemical precipitate, but my experiments in this department have not yet been sufficiently extended to authorize me in recommending any particular process.

191. The object of the observer may however be altogether different, and he may wish to extend the spectrum as far as possible, for the purpose of viewing the fixed lines belonging to the invisible part beyond the extreme violet, or making experiments on the invisible rays. For this purpose it would be proper to employ a clear and highly sensitive solid or fluid. A weak solution of sulphate or phosphate of quinine would do very well, or a weak decoction of the bark of the horse-chestnut (no doubt a solution of pure esculine would be better), or an alcoholic solution of the seeds of the *Datura stramonium*. But perhaps the most convenient thing of all would be a slab of glass coloured yellow by oxide of uranium. This would be always ready, and in point of sensibility the glass does not seem to yield to any of the solutions above mentioned, at least so far as relates to those rays which are capable of passing through glass\*.

192. In making experiments on the invisible rays, it is well to get rid, as far as possible, of the glare arising from the bright part of the spectrum, and therefore a clear solid or solution is preferable to an opaque screen. If it be desired to show the fixed lines in the visible and invisible parts of the spectrum at the same time, a screen may be employed consisting of paper washed with a moderately strong solution of sulphate of quinine, or an alcoholic solution of stramonium seeds. Turmeric paper is not, I think, quite so good for showing the fixed lines of very high refrangibility, but is at least equally good for the extreme violet and for the rays a good distance further on, especially if it has been washed with a solution of tartaric acid. It is likely that many other acids would do as well. Very excellent screens might probably be prepared by washing paper with a solution of esculine, or even of the bark of the horse-chestnut†, or by covering pasteboard with yellow uranite reduced to fine powder, and made to adhere by a weak solution of pure gum Arabic; but these I have not tried.

\* See note F.

† See note G.

*Application of internal dispersion to demonstrating the course of rays.*

193. Solutions of quinine have already been employed for this purpose, and a weak decoction of the bark of the horse-chestnut appears to be decidedly better. But the effect is immensely improved by using absorbing media to cut off all the rays belonging to the bright part of the visible spectrum. A deep blue glass will answer very well for this purpose if its faces be even, so as not to disturb the regularity of the refraction. The appearance of the general pencil refracted through a rather large lens, with its caustic surface, its geometrical focus, &c., is singularly beautiful when exhibited in this way, on account of the perfect continuity of the light, and the delicacy with which the different degrees of illumination belonging to different parts of the pencil are represented by the different degrees of brightness of the dispersed light. The solution should be contained in a vessel with plane sides of glass, and ought to be very weak, or else only the part of the pencil which lies near the surface by which the light enters will be properly represented.

*Application of internal dispersion to the determination of the absorbing power of media with respect to the invisible rays beyond the violet, and the reflecting power of surfaces with respect to those rays.*

194. Hitherto no method has been known by which the absorbing power of a medium with respect to these rays could be determined for each degree of refrangibility in particular, except that which consists in taking a photographic impression of a pure spectrum, the light forming the spectrum having been transmitted through the substance to be examined. It is needless to remark how troublesome such a process is when contrasted with the mode of determining the absorption which media exercise on the visible rays. But the phenomenon of internal dispersion furnishes the philosopher, so to speak, with *eyes to see the invisible rays*, so that the absorbing power of the medium with respect to these rays may be instantly observed. For this purpose it is sufficient to form a pure spectrum, using instead of a screen a highly sensitive fluid or solid, such as one of those mentioned in Art. 191, and to hold before it the medium to be examined, or else to place the medium over the whole or a part of the slit.

195. In this way the transparency of glass coloured yellow by oxide of silver with respect to the violet rays and some of those still more refrangible, which has been remarked by Sir JOHN HERSCHEL\*, may be at once observed. A set of green glasses were found to be very variable in the mode in which they absorbed the invisible rays, some absorbing the more refrangible of the rays capable of affecting a dilute solution of sulphate of quinine and transmitting the less refrangible, others absorbing the less and transmitting the more refrangible, and others again absorbing them all. These rays were absorbed by solutions of chromate and bichromate of potash so weak as to be almost colourless. A thickness of about a quarter of an inch of sulphuret of

\* Philosophical Transactions for 1840, p. 39.

carbon was sufficient to absorb all the rays beyond  $Hk1$ , so that a hollow prism filled with this fluid would be useless in experiments on these rays. It should be remarked that the sulphuret of carbon employed was not yellow from dissolved sulphur, but apparently as colourless as water.

196. To determine qualitatively the reflecting power of a polished surface with respect to the invisible rays of each particular degree of refrangibility, it would be sufficient to form a pure spectrum as usual, reflect the rays sideways before they come to the focus of the larger lens, place a sensitive medium to receive them, and compare the effect with that produced on the same medium when the rays are allowed to fall directly upon it.

*Effect of different Flames.*

197. Want of sunlight proved to be such an impediment to the pursuit of these researches that I was induced to try some bright flames, with the view of obtaining some convenient substitute. Candle-light is very ill adapted to these experiments. The flame of a camphene-lamp proved no better, perhaps rather worse, for it abounds so much in rays belonging to the bright part of the spectrum that the glare of the light prevents all observation of faint objects; and the flame does not appear to be rich in invisible rays in anything like the proportion in which it is rich in visible ones. The flame of nitre burning on wood or charcoal produced a very good effect, exhibiting, when the combustion was most vivid, a copious dispersive reflexion in a weak solution of sulphate of quinine contained in a bottle held near it. The tint of the dispersed light appeared to be not quite the same as that given by daylight, but to verge a little towards violet. However, I do not place very strong reliance on the judgment of the eye under such circumstances. A still stronger dispersive reflexion was produced by a flash of gunpowder. The tint in this case appeared to be the same as that seen by daylight.

198. While engaged in some of these experiments on bright flames, I was surprised by discovering the strong effect produced by the flame of a spirit-lamp, the illuminating power of which is so feeble. When this flame was held close to a bottle containing sulphate of quinine, a very distinct dispersive reflexion was exhibited. The same was the case with several other sensitive solutions. However, the full effect of the flame is not thus exhibited, because a considerable portion of the rays which it emits is stopped by glass. It is best observed by pouring the solution into an open vessel, such as a wine glass or tumbler, holding the flame immediately over it, and placing the eye in or very little below the plane of the surface. In this way nothing is interposed between the flame and the fluid, except an inch or two of air, the absorption produced by which, it is presumed, is insensible; and the plane strata, parallel to the surface, into which the illuminated portion of the fluid may be conceived to be divided, are all projected into lines, whereby the intensity of the blue light is materially increased. It is to be observed further, that if the eye be held a

little below the plane of the surface, there enters it, not only the light coming directly from the blue stratum itself, but also that coming from its image formed by total internal reflexion. This mode of observation has already been employed by Sir JOHN HERSCHEL in the case of sunlight. As it is frequently useful in these researches it will be convenient to have a name for it, and I shall accordingly speak of it as the method of observing by *superficial projection*.

199. The opacity of a solution of sulphate of quinine appears to increase regularly and rapidly with the refrangibility of the light. Hence we may form an estimate of the refrangibility of any light by which the solution may be affected, by observing the degree in which the illumination is concentrated in the neighbourhood of the surface. For this purpose it is essential to employ a weak solution, since otherwise streams of invisible light of various degrees of refrangibility produce each their full effect in strata so very narrow, that they cannot be distinguished by the breadth of the stratum. Now to judge by the great concentration of the illumination produced by a spirit-lamp, even in the case of an extremely weak solution, as well as by the considerable degree in which the active rays were intercepted by glass, these rays, taken as a whole, must have been of very high refrangibility, such as to place them among the most refrangible of the fixed lines represented in the map, or perhaps even altogether beyond them. In making observations on the solar spectrum, it was plain that the prisms were by no means transparent with respect to the rays belonging to the group *p* of fixed lines. Yet these rays, before they produced their effect, had to pass twice through the plate-glass belonging to the mirror (except so far as regards the rays reflected at the first surface), then through three prisms, though to be sure as close as possible to the edges, then through a lens by no means very thin, and lastly, through the side of the vessel containing the fluid. Such a train of glass would be sufficient materially to weaken, if not even wholly to cut off the active rays coming from the flame of a spirit-lamp.

200. The flame of naphtha produces nearly the same effect as that of alcohol. The flame of ether is not so good; but whether this arises solely from its richness in visible rays, which only produce a glare, or likewise from a comparative poverty in highly refrangible invisible rays, it is not easy to say. The flame of hydrogen produces a very strong effect. The invisible rays in which it so much abounds, taken as a whole, appear to be even more refrangible than those which come from the flame of a spirit-lamp. In making some observations with the flame of hydrogen, when the gas was nearly exhausted, so that the flame was reduced to a roundish knob no larger than a sweet pea, and giving hardly any light, it was found still to produce a very marked effect when held over the surface of a solution of sulphate of quinine. The flame of sulphuret of carbon produces on most objects a much stronger effect than that of alcohol. It exhibits distinctly the blue light dispersed close to the surface of a solution of guaiacum in alcohol, which the flame of alcohol does not. It appears then that the flame of sulphuret of carbon is rich in invisible rays of such a

refrangibility as to place them among the groups of fixed lines  $m, n$ , or a little beyond, since when a solution of guaiacum is examined in the solar spectrum, it is found that that is the region in which the blue dispersed light is produced. The blue light dispersed by a solution of guaiacum may also be seen by using the blue flame of sulphur burning feebly. The poverty of the flame of a spirit-lamp, not only with respect to visible rays, but also with respect to invisible rays, except those of very high refrangibility, accounts for the circumstance that it does not exhibit, or at least hardly at all exhibits, the blue light dispersed by fluor-spar.

*Mode of determining, by means of the light of a spirit-lamp, the transparency of bodies with respect to the invisible rays of high refrangibility.*

201. If the body be a solid, and be bounded by parallel surfaces, its transparency with regard to these rays is easily tested. For this purpose it is sufficient to hold the flame of a spirit-lamp a little way above the surface of a weak solution of sulphate of quinine contained in an open vessel in a dark room, and then, placing the eye so as to see the dispersed light in projection, alternately to interpose and remove the plate to be examined.

202. On examining in this way various specimens of glass, I found none which did not show evident defects of transparency. The purest specimens of plate-glass appeared, I think, to be the least defective. I cannot say whether the observed defects of transparency were due to the essential ingredients of the glass, or to accidental impurities. It is possible that glass made with chemically pure materials might be transparent\*. I believe that a mere trace of peroxide of iron, or of sulphuret of soda or potassa, would be sufficient to impair materially the transparency of glass with respect to these rays, and such impurities are very likely to be present. Quartz, however, appeared to be perfectly transparent, the active rays passing through the thickness of one or two inches, whether parallel or perpendicular to the axis, without any perceptible loss. The contrast between quartz and mica was very striking, for a plate of mica no thicker than paper produced a very sensible diminution in the illumination.

203. For the purpose of observing fluids, I procured two vessels consisting of sections of a wide glass tube, about an inch long, closed at one end with a disc of quartz. I shall call these for brevity quartz vessels, though of course the bottom is the only part in which there is any occasion to use quartz. When a fluid is to be examined it is poured into a quartz vessel, and then the vessel with its fluid contents is examined in the manner of a solid plate, as described in Art. 201. On account of the perfect transparency of quartz, the fluid is as good as suspended in air. When a

\* Some specimens of glass belonging to Dr. FARADAY's experiments, which from the absence of colour and of internal dispersion seemed hopeful, could not be examined for transparency, on account of their irregular figure; and as they were only lent to me by a friend, I did not feel myself at liberty to get them cut and polished.

quartz vessel was partly filled with water, the addition of a very small quantity of nitrate of iron was sufficient to cause the absorption of the active rays. The solution was so weak as to be almost colourless when viewed through the thickness through which the rays would have to pass. A solution of perchloride of iron had a similar effect. These fluids I had specially examined by sunlight, and had not found in them the least trace of internal dispersion. When a fluid exhibits internal dispersion, it is almost always very opaque with regard to rays of high refrangibility, as is shown, without any special experiment, in the course of the observations by which the internal dispersion is exhibited; but it by no means follows conversely, that when a fluid is very opaque with regard to these rays, though nearly transparent with regard to the visible rays, it exhibits the phenomenon of internal dispersion.

204. I have little doubt that the solar spectrum would be prolonged, though to what extent I am unable to say, by using a complete optical train in every member of which glass was replaced by quartz. Such a train would be rather expensive, but would not involve any particular difficulty of execution. If solid prisms of quartz were used, half of the incident light would be lost, on account of the double refraction of the substance, unless the prisms were cut in a particular manner, which however would seem likely to involve some difficulties, both in the execution and in the observations. But hollow prisms holding fluids might be employed, having the two faces across which the light has to pass made of quartz plates. For a reason already mentioned, sulphuret of carbon cannot be employed for filling the prisms, and the dispersive power of water is very low, but there appears to be no objection to the use of a solution of some colourless metallic salt. At least saturated solutions of sulphate of zinc and of acetate of lead, the only salts I have tried with this view, showed no defects of transparency when examined in quartz vessels by means of the flame of a spirit-lamp and a solution of sulphate of quinine\*.

*Effect of Hydrochloric Acid, &c. on Solutions of Quinine. Optical evidences of combination in other instances.*

205. Sir JOHN HERSCHEL, in his interesting paper already so often referred to, observes that it is only acid solutions of quinine which exhibit the peculiar blue colour, and that among different acids the muriatic seems least efficacious (page 145).

For my own part I have tried solutions of quinine (not disulphate) in dilute sulphuric, phosphoric, nitric, acetic, citric, tartaric, oxalic, and hydrocyanic acids, and also in a solution of alum. In all these cases the blue colour of the dispersed light was plainly seen by ordinary daylight, especially when the fluid was examined by superficial projection. It was not easy to say which solution answered best, but I am inclined to think that in which phosphoric acid was used.

206. But when quinine was dissolved in dilute hydrochloric acid the blue colour was not exhibited, not even when the fluid was held in the sunlight, and examined by superficial projection. Certain theoretical views led me to regard this as an evi-

\* See note H.

dence of a more intimate union between quinine and hydrochloric acid than between quinine and the acids first mentioned, and to try whether the addition of hydrochloric acid to the solutions mentioned in the preceding paragraph would not destroy the blue colour. On trial this proved to be actually the case, so that even sulphuric acid is incapable of developing the blue colour in a solution of quinine in hydrochloric acid.

207. That the quinine was not decomposed when the blue colour due to sulphate of quinine was destroyed by hydrochloric acid, but only differently combined, was shown by adding a solution of carbonate of soda, which produced a white precipitate; and when this was collected on a filter, washed, and redissolved in dilute sulphuric acid, it exhibited the blue colour as usual.

208. The addition of a solution of common salt, instead of hydrochloric acid, to the solutions mentioned in Art. 205, likewise destroyed the blue colour. In the case of sulphuric acid this is only what might have been confidently anticipated; but we should not perhaps have expected that quinine in combination with a weak acid, such as citric, would decompose hydrochlorate of soda, giving rise to citrate of soda and hydrochlorate of quinine; yet this appears to be the nature of the reaction.

209. It might perhaps be supposed that the sulphuric acid was only partially expelled from sulphate of quinine by hydrochloric acid, and that the salt in solution was really a sort of double salt, in which the same base, quinine, was combined with sulphuric and hydrochloric acids in atomic proportion. But if so, it is probable, though not certain, that the same salt would be formed on adding hydrochloric acid to a solution of disulphate of quinine, even though the quantity were not sufficient to combine with the whole of the disulphate. On this supposition, if hydrochloric acid were added by small quantities at a time to a solution of disulphate of quinine, the blue colour ought not to be developed; and when acid enough had been added it ought to be incapable of being developed by the addition of sulphuric acid; whereas, if the whole of the sulphuric acid be expelled by hydrochloric acid, the blue colour ought to be first developed, by the conversion of a portion of the disulphate of quinine into a sulphate, and then destroyed, on the addition of more acid, by the conversion of the sulphate into a hydrochlorate. On trying the experiment with a solution of disulphate of quinine in warm water, it was found that the blue colour was actually first developed and then destroyed.

210. A practical conclusion which seems to follow from these results is, that in the employment of quinine in medicine it is of little consequence whether the sulphate, phosphate, acetate, or hydrochlorate be used, since the first three salts would be immediately converted by the common salt in the body into the hydrochlorate, and the small quantity of a neutral salt of soda resulting from the double decomposition could hardly, one would suppose, be worth considering. However, the common quinine is associated with cinchonine, the reactions of which may be different. According to Sir JOHN HERSCHEL, the latter alkaloid does not exhibit the blue colour, and therefore the optical tests do not apply to it. If it be desired to obtain a soluble



salt of quinine which shall not be converted by common salt, by double decomposition, into a hydrochlorate, it must apparently be sought for among the combinations of quinine with very weak acids, the affinity of which for soda does not much help that of hydrochloric acid for quinine. It seems likely enough that such salts may exist; for though acetate or citrate of quinine decomposes hydrochlorate of soda, hydrochlorate of quinine is decomposed by carbonate of soda; and it is probable that many vegetable acids behave like the carbonic in this respect.

211. The blue dispersion of a solution of sulphate of quinine is destroyed by hydrobromic and hydriodic acids just as by hydrochloric. In the experiment, solutions of bromide and iodide of potassium were used; but as a considerable excess of sulphuric acid was purposely added to the solution of quinine, the potassa introduced would merely remain inert in the solution as a sulphate, without impeding the observation. The same experiment was tried with phosphate of quinine with the same result.

212. It is stated in TURNER'S Chemistry, that the play of colours observed in solutions of polychrome (*i. e.* esculine) is destroyed by acids, and heightened by alkalies. The destruction, or at least almost complete destruction, of the blue colour due to dispersed light in a decoction of the bark of the horse-chestnut, which is produced by acids, is readily observed; but I could not perceive that the addition of alkalies in the first instance to a fresh solution made any difference one way or other. If the blue colour had previously been destroyed by an acid, it was restored by the alkali. If the horse-chestnut had never been examined chemically, these observations alone would indicate that in all probability the principle to which the blue colour was due was capable of entering into firm combination with acids, but did not combine with alkalies. It is, in fact, as we know, a vegetable base.

213. A solution of nitrate of uranium in ether is insensible, as if some of the elements of the ether entered into firm combination with the oxide of uranium. In connexion with this circumstance, it is rather remarkable, that although the ether passes off by evaporation when the solution is left to itself in an open vessel, if heat be applied chemical action sets in, and the residue consists chiefly of a salt which has all the appearance of oxalate of uranium. This salt, when washed and examined in the moist state, without very great concentration of light, was found to be insensible\*.

214. It is rare to meet with solutions so highly sensitive as those of quinine and esculine, but similar observations may be made on a great number of solutions, by employing suitable methods. The most searching method consists in forming a bright and tolerably pure spectrum, by transmitting the sun's light through a very broad slit, or even leaving out the slit altogether. It is desirable to use a lens of only moderate focal length in connexion with the prisms. The solution having been placed in the spectrum, the acid, or other agent whose reactions it is desired to study,

\* See note I.

is to be added, and the effect, if any, observed. It is usually advantageous to cover the slit with a blue glass, or similar absorbing medium; but sometimes effects take place in the bright part of the spectrum, which is intercepted by such a medium. When false dispersion abounds, it is well to look down on the fluid through a Nicol's prism, so as to stop all light which is polarized in the plane of reflexion.

*Negative results with reference to a mutual action of the rays incident on sensitive solutions.*

215. The antagonistic effects of the more and less refrangible rays, which have been observed in certain phenomena, induced me to try whether anything of the kind could be perceived in the case of internal dispersion. The following arrangement was adopted for putting this question to the test of experiment.

A tumbler was filled with a very dilute solution of sulphate of quinine, and placed in a pure spectrum. As usual, the illuminated portion of the fluid consisted of two distinct parts, one the blue beam of truly dispersed light, corresponding to the highly refrangible rays, the other the beam reflected from motes, exhibiting the usual prismatic colours, and corresponding to the brighter of the visible rays. The fluid was nearly free from motes, so that the first beam was by far the brighter of the two; and the second beam, without being bright enough at all to interfere with the observation, was useful as serving to point out where the red, yellow, &c. rays lay. A flat prism, having an angle of about  $130^\circ$ , was then held in front of the vessel, with its edge vertical, and situated in the more refrangible part of the visible rays. The rays forming the two beams were thus bent in opposite directions, and the beams made to cross each other within the fluid; and by turning the prism a little in both directions in azimuth, that is, round an axis parallel to the incident rays, it was easy to make sure that the beams did actually cross. But not the slightest perceptible difference in the blue beam was made by the passage of the red and other lowly refrangible rays across it.

216. Certain theoretical views having led me to regard it as doubtful whether the intensity of light internally dispersed was proportional to the intensity of the incident rays, other circumstances being the same, I was induced to try the following experiment.

The sun's light was reflected horizontally through a large lens, which was covered by a screen containing two moderately large round holes, situated in the same horizontal plane, and a good distance apart. The beams coming through the two holes converged of course towards the focus of the lens, and at the same time contracted in width, and became brighter from the concentration of the light. For our present purpose, they may be regarded as cylindrical beams converging towards the focus of the lens. When they had approached each other sufficiently, they were transmitted through a blue ammoniacal solution of copper, contained in a vessel with parallel sides. The object of this was of course to absorb all the bright visible rays, which

would not only be useless for exciting the solution which it was meant to try, but would materially hinder the observation by the glare which they would produce. The beams were then admitted into a vessel containing a decoction of the bark of the horse-chestnut, greatly diluted with water. In passing through the fluid they produced two blue beams of truly dispersed light, which converged towards a point a little way outside the vessel. A flat prism, with an angle of about  $150^\circ$ , was then held in front of the vessel, with its edge vertical, and situated between the incident beams. The blue beams of dispersed light were thus made to cross within the fluid; and by moving the prism in azimuth, it was easy to make one beam either fall above the other, cross it, or fall below it. Now on looking down from above with one eye only, and moving the prism backwards and forwards in azimuth, I could not perceive the slightest difference of illumination, according as the blue beams actually crossed each other, or were merely seen projected one on the other. In this experiment, then, it appeared that one beam of incident rays produced as much additional dispersed light in a portion of fluid already excited by the other beam, as it was capable of producing in a similar portion of fluid not otherwise excited.

*Effect of an electric spark. Nature of its phosphorogenic rays.*

217. For the use of the apparatus with which the following experiments were made, I am indebted to the kindness of Professor CUMMING.

An electric spark produces an internal dispersion of light in a very striking manner in the case of an extremely dilute solution of sulphate of quinine. Having prepared a solution so weak, that when it was examined by superficial projection by the light of a spirit-lamp, nothing was seen but a pale gleam of light extending a good way into the fluid, and not only not confined to the surface, but not even showing any particular concentration in the neighbourhood of the surface, I placed it so as to be illuminated by the sparks from the prime conductor of an electrifying machine, which passed at no great distance over the surface. A very marked internal dispersion was produced, but the nature of the effect depended in a good measure on the character of the spark. A feeble branched spark, giving but little light, and making little noise, produced an illumination extending to a considerable depth, and very much stronger than that occasioned in the same solution by the flame of a spirit-lamp. The rays by which this was produced passed in a great measure through a plate of glass interposed between the spark and the surface of the fluid. But a bright linear spark, making a sharp crack, produced an illumination almost confined to an excessively thin stratum adjacent to the surface of the fluid; and the rays by which this was produced were cut off by glass, though transmitted through quartz. The same was the case with the discharge from a Leyden jar, which produced a bright light almost confined to the surface\*.

218. The opacity of a solution of sulphate of quinine appears to increase regularly

\* See note J.

and rapidly with the refrangibility of the rays incident upon it. Hence we are led to the conclusion that a strong electric spark is excessively rich in invisible rays of extremely high refrangibility. Glass is opaque with respect to these rays, but quartz transparent.

219. It is known that the phosphorogenic rays of an electric spark, at least those which affect CANTON's phosphorus, pass very freely through quartz, but are stopped by a very moderate thickness of glass. This alone, after what has been already mentioned, would lead us to suppose that the phosphorogenic rays coming from such a spark are merely rays of very high refrangibility. If so, they ought to be intercepted by a very small quantity of a substance known to absorb such rays with energy.

After having made some experiments on the production of phosphorescence in CANTON's phosphorus by means of an electric discharge, and observed how the influence of the discharge was transmitted through quartz and stopped, or almost entirely stopped, by glass, I felt confident that my own observations were comparable with those of others. A small portion of the phosphorus was then placed on card, covered by an empty quartz vessel, and had the discharge of a Leyden jar passed over it. The phosphorescence was powerfully excited, being visible in a room which was by no means quite dark; and when the card was carried into a dark place, the phosphorescent light remained plainly visible for a good while. The experiment was then repeated with a fresh portion of the same phosphorus, the vessel this time containing water. The phosphorescence was produced as before, though not I think so copiously. But on taking a fresh portion of the phosphorus, and substituting for water a very dilute solution of sulphate of quinine, the influence of the spark was arrested, and the phosphorus was not rendered luminous. It was found that a solution containing only about one part of quinine in 10,000, with a depth of half an inch, was sufficient to prevent the generation of phosphorescence.

220. This result, it seems to me, would be sufficient, were proof wanting, to show that no part of the effect is attributable *directly* to the electrical disturbance. The effect produced when the phosphorus is at the distance of an inch or so from the points of the discharger seems exactly the same as when it is nearer, being merely somewhat weaker, as would naturally be expected, whatever view were taken of the nature of the influence. But at the distance of an inch, the influence of the spark, though it passes freely through quartz and water, is cut off by adding to the water an excessively small quantity of sulphate of quinine. It cannot be supposed that the electrical relations of the medium, or its permeability to electrical attractions and repulsions, are utterly changed by such an addition; while, on the other hand, the result is in perfect conformity with what we know respecting the stoppage of radiations by absorbing media. However, the principal object of the experiment was not to confirm the view which makes the influence of the spark to consist in the rays which emanate from it, a view which I suppose is pretty generally adopted, but to

investigate more fully the nature of these rays. Enough has, I think, been adduced to show that they are merely rays which there is no reason to suppose are physically different from those of light, but quite the contrary, and which are of very high refrangibility, and are therefore invisible, since they fall far beyond the limits of refrangibility within which the retina is affected. Indeed, it seems very likely that the highly refrangible rays never reach the retina, but are absorbed by the coats of the eye\*. Hence the phenomena relating to the phosphorescence produced by an electric discharge afford no countenance to the supposition that it is possible to divide rays of a given refrangibility into phosphorogenic, chemical, luminous, &c. Of course the most unexceptionable mode of determining the refrangibility of the phosphorogenic rays would be by actual prismatic decomposition, but this would require the employment of a quartz train.

*Points of resemblance and contrast between internal dispersion and phosphorescence.*

221. As the term *phosphorescence* has been applied to several different phenomena, I must here explain that I mean the spontaneous exhibition of a soft light, independently of chemical changes, which some substances exhibit for a time after having been exposed to the sun's rays, or to an electric discharge, or to light from some other sources.

In many respects the two phenomena have a strong resemblance. Thus, the general features of internal dispersion cannot be better conceived than by regarding the sensitive medium as self-luminous while under the excitement of the active rays. Again, it is well known that the rays of the solar spectrum by which the phosphorescence of CANTON'S phosphorus, sulphuret of barium, and other phosphori, is produced, are those of high refrangibility, as well as the invisible rays beyond; and these are precisely the rays which in the great majority of cases are most efficient in producing internal dispersion. I do not however know how far it may be true that when phosphorescence is excited by homogeneous light the refrangibility of the incident light is a superior limit to the refrangibilities of the component parts of the light emitted. Indeed, according to Professor DRAPER, when the phosphorescence of CANTON'S phosphorus is excited by the rays from incandescent lime, the active rays belong to the red extremity of the spectrum†. If this result be confirmed, it follows that the most striking law relating to internal dispersion is not obeyed in the case of phosphorescence.

In the same paper Professor DRAPER remarks, "Some time ago I determined the refrangibility of the rays of an electric spark which excite phosphorescence in sulphuret of lime; they are found at the violet extremity of the spectrum." In what way Professor DRAPER determined the refrangibility of rays with respect to which glass is so opaque, he does not give the least hint. Being perfectly in the dark as to the evidence on which the conclusion is based, I cannot accept it in contradiction to

\* See note K.

† Philosophical Magazine, vol. xxvii. (Dec. 1845) p. 436.

my own experiments. Perhaps, however, "at the violet extremity" may mean nothing more than somewhere in the highly refracted region beyond the visible rays. If so, Professor DRAPER's statement is in accordance with my own conclusions.

222. When one part of a phosphorus has been excited, the phosphorescence is found gradually to extend itself to the neighbouring parts. In this respect a substance which exhibits internal dispersion presents a striking contrast. The finest fixed lines of the spectrum are seen sharply defined, whether in a solution, or in a clear solid, or on a washed paper.

223. Of course, theoretically, there ought, to a certain extent, to be a communication of illumination from one part of a sensitive fluid to another, on account of the light which is twice, three times, &c. dispersed. This however must be excessively small; for the mean refrangibility of the dispersed light is usually much lower than the refrangibility of the active light, perhaps lower than that of any light capable of exciting the solution. However, generally some few of the dispersed rays would have a refrangibility sufficiently high to be dispersed again. But practically the intensity of the light twice dispersed in this manner would be so very small that it may safely be altogether disregarded.

224. But by far the most striking point of contrast between the two phenomena, consists in the apparently instantaneous commencement and cessation of the illumination, in the case of internal dispersion, when the active light is admitted and cut off. There is nothing to create the least suspicion of any appreciable duration in the effect. When internal dispersion is exhibited by means of an electric spark, it appears no less momentary than the illumination of a landscape by a flash of lightning. I have not attempted to determine whether any appreciable duration could be made out by means of a revolving mirror.

225. There appears to be no relation between the substances which exhibit a change of refrangibility and those which phosphoresce, either spontaneously, or on the application of heat. Thus the sulphurets of calcium and barium, on being examined for internal dispersion, were found to be insensible, as was also Iceland spar. The last substance phosphoresced strongly on the application of heat. So far as was examined, the minerals which did exhibit a change of refrangibility showed no special disposition to phosphoresce. Sir DAVID BREWSTER has remarked, that a specimen of fluor-spar which exhibited a blue light by internal dispersion, exhibited when heated a blue phosphorescent light; but this appears to have been merely a casual coincidence\*.

*On the Cause of True Internal Dispersion, and of Absorption.*

226. In considering the cause of internal dispersion, we may I think at once discard all supposition of reflexions and refractions of the vibrations of the luminiferous ether among the ultimate molecules of bodies. It seems to be quite contrary

\* Report of the Meeting of the British Association at Newcastle in 1839, p. 11.

to dynamical principles to suppose that any such causes should be adequate to account for the production of vibrations of one period from vibrations of another.

All believers, I suppose, in the undulatory theory of light are agreed in regarding the production of light in the first instance as due to vibratory movements among the ultimate molecules of the self-luminous body. Now in the phenomenon of internal dispersion, the sensitive body, so long as it is under the influence of the active light, behaves as if it were self-luminous. Nothing then seems more natural than to suppose that the incident vibrations of the luminiferous ether produce vibratory movements among the ultimate molecules of sensitive substances, and that the molecules in turn, swinging on their own account, produce vibrations in the luminiferous ether, and thus cause the sensation of light. The periodic times of these vibrations depend upon the periods in which the molecules are disposed to swing, not upon the periodic time of the incident vibrations.

227. But in the very outset of this theory an objection will probably be urged, that it is quite as much contrary to dynamical principles to suppose the periodic time of the ethereal vibrations capable of being changed through the intervention of ponderable molecules as without any such machinery. The answer to this objection is, that such a notion depends altogether on the applicability of a certain dynamical principle relating to indefinitely small motions, and that we have no right to regard the molecular vibrations as indefinitely small. The excursions of the atoms may be, and doubtless are, excessively small compared with the length of a wave of light; but it by no means follows that they are excessively small compared with the linear dimensions of a complex molecule. It is well known that chemical changes take place under the influence of light, especially the more refrangible rays, which would not otherwise happen. In such cases it is plain that the molecular disturbances must not be regarded as indefinitely small. But vibrations may very well take place which do not go to the length of complete disruption, and yet which ought by no means to be regarded as indefinitely small. Furthermore, it is to be observed that if in the cases of indefinitely small molecular displacements the forces of restitution be not proportional to the displacements, the principle above alluded to will not be applicable however small the disturbance may be; and if in the expressions for the forces of restitution the terms depending on first powers of the displacements (supposed finite), though not absolutely null, be very small, the principle will not apply unless the molecular excursions be extremely small indeed. In consequence of the necessity of introducing forces not proportional to the displacements, it would be very difficult to calculate the motion, even were we acquainted with all the circumstances of the case, whereas we are quite in the dark respecting the actual data of the problem. But certainly we cannot affirm that in the disturbance communicated back again to the luminiferous ether none but periodic vibrations would be produced, having the same period as the incident vibrations. Rather, it seems evident that a sort of irregular motion must be produced in the molecules, periodic only in the

sense that the molecules retain the same mean state; and that the disturbance which the molecules in turn communicate to the ether must be such as cannot be expressed by circular functions of a given period, namely, that of the incident vibrations.

228. It is very remarkable with what pertinacity a particular mode of internal dispersion attaches itself to a particular chemical substance. Thus the singular dispersion of a red light exhibited by the green colouring matter of leaves is found in a green leaf, or in a solution of the green colouring matter in alcohol, ether, sulphuret of carbon, or muriatic acid. The dispersion exhibited by nitrate of uranium is found in a solution of the salt in water, as well as in the crystals themselves, which are doubly refracting. In all probability therefore the molecular vibrations by which the dispersed light is produced are not vibrations in which the molecules move among one another, but vibrations among the constituent parts of the molecules themselves, performed by virtue of the internal forces which hold the parts of the molecules together. It is worthy of remark that it is chiefly among organic compounds, the ultimate molecules of which we are taught by chemistry to regard as having a complicated structure, that internal dispersion is found. It is true that peroxide of uranium furnishes many examples of internal dispersion; but then the anhydrous peroxide is itself insensible, it is only some of the compounds into which it enters that are so remarkably sensitive; and the chemical formulæ of these compounds, so far as they are known, are not by any means extremely simple, although it is true that they may not be more complicated than formulæ relating to other oxides. Why this particular oxide should be disposed to enter into tottering combinations I do not pretend even to conjecture; but it seems not a little remarkable that peroxide of uranium, which is so peculiar with respect to its optical properties, should also present some singularities in its mode of chemical combination, which led M. PELIGOT to regard it as the protoxide of a compound radical.

229. We are, I conceive, at present far from an explanation of the phenomena of internal dispersion in all their details. They appear to be associated with the inmost structure of chemical molecules, to such a degree as to throw even the phenomena of polarization into the shade. In this respect, indeed, absorption seems superior to polarization, since most of the phenomena of polarization refer rather to the state of crystalline aggregation of the molecules than to their constitution; but the phenomena of internal dispersion appear to be much more searching than those of absorption. There is one law however relating to internal dispersion so striking and so simple, that it seems not unreasonable to look for an explanation of it; I allude to that according to which the refrangibility of light is always lowered in the process of dispersion. I have not hitherto been able altogether to satisfy myself respecting a dynamical explanation of this law, but the following conjectures will not perhaps be deemed altogether unworthy of being mentioned.

230. Reasons have already been brought forward for regarding the molecular vibrations as performed under the influence of forces not proportional to the dis-



placements. For simplicity's sake, let us suppose for the present the parts of the forces of restitution depending upon first powers of the displacements to be absolutely null. Then, when a molecule is disturbed, its atoms will be acted on by forces depending upon the second and higher powers of the displacements. These forces must tend to restore the atoms to their mean positions; otherwise the equilibrium would be unstable, and the atoms would enter into new combinations, either with one another, or with the atoms of the surrounding medium; so that, in fact, such compounds could never be formed. The condition of stability would require the parts of the forces depending upon squares of the displacements to vanish, but this is a point which need not be attended to, all that is essential to bear in mind being, that we have forces of restitution varying in a higher ratio than the displacements. If the parts of the forces of restitution which depend upon first powers of the displacements, though not absolutely null, be very small, the remaining parts must still be such as to tend to restore the atoms to their positions of equilibrium; otherwise the stability of the molecule, though not mathematically null, would be so very slight, that such compounds would probably never form themselves, but others of more stability would be formed instead. Or, even were such unstable compounds formed, they would probably be decomposed on attempting to excite them in the manner in which sensitive substances are excited in observing the phenomena of internal dispersion; so that whether they exist or not, they may be set aside in considering these phenomena.

231. Now when vibrations are performed under the action of forces which vary in a higher ratio than the displacements, the periodic times are not constant, but depend upon the amplitudes of vibration, being greater or less according as the amplitudes are less or greater. Suppose the molecular and ethereal vibrations already going on, and imagine the amplitudes of the former kept constant by the application of external forces. According to the value of the epoch of the vibrations of a particular molecule, the ethereal vibrations will tend, in the mean of several successive undulations, to augment or to check the vibrations of the molecule. For some time there will be a tendency one way, then for some time a tendency the other way, and so on, the opposite tendencies balancing each other in the long run. The lengths of the times during which the tendency lies in one direction, will depend upon the periodic times of the molecular and ethereal vibrations, being on the whole greater or less according as the two periodic times are more or less nearly equal. But since no external forces actually act to keep the amplitudes constant, when the ethereal vibrations are favourable to disturbance the molecule is further disturbed, and therefore its periodic time is diminished; and when they are favourable to quiescence the disturbance of the molecule is checked, and therefore its periodic time is increased. If, then, the ether be vibrating more rapidly than the molecule, when the action is favourable to disturbance the periodic time of the molecular vibrations is rendered more nearly equal to that of the ethereal vibrations, and therefore the time

during which the action is favourable to disturbance is prolonged; but when the action is favourable to quiescence, the effect is just the reverse. Hence, on the whole, there is a balance outstanding in favour of disturbance. But if the ether be vibrating more slowly than the molecule, it appears from similar reasoning that there will be a balance the other way. Hence it is only when the periodic time of the ethereal vibrations is less than that of the molecular, that the latter vibrations can be kept going by the former.

232. But it will probably be objected to this explanation, that when a periodic disturbing force affects the mean motion of a planet, the mean motion is a maximum, not when the force tending to augment it is a maximum, but at a time later by a quarter of the period of the force, namely, when the force vanishes in changing sign; and that in a similar manner the change in the periodic time of the vibrations of a disturbed molecule will affect equally the duration of the time during which the action is favourable to increased disturbance, and that during which it is favourable to quiescence, or more exactly will not alter either, since the effects in the first and second halves of those times will neutralize each other. The answer to this objection is, that we must not treat a molecule as if it were isolated, like a heavenly body, since it is continually losing its motion by communication, perhaps to neighbouring molecules, but at any rate to the luminiferous ether; for without a communication of the latter kind there would be no dispersed light. Hence we must consider the *immediate* tendency of the disturbing forces rather than their tendency in the long run.

233. When a molecule itself vibrates in an irregularly periodical manner, the vibrations which it imparts to the ether are of course of a similar character. The resolution of these into vibrations corresponding to different degrees of refrangibility, involves some very delicate mathematical considerations, into which I do not propose to enter. But without this it is evident that when the ether is agitated by the vibrations of an immense number of molecules, in all possible states as regards amplitude, and consequently periodic time of vibration, the disturbance of the ether must consist of a mixture of periodic vibrations, having their periods comprised between the greatest and least of those belonging to the molecular vibrations; and corresponding to these different periods there will be portions of light of different degrees of refrangibility found in the dispersed beam. These refrangibilities will range between two limits, an inferior limit equal to the refrangibility corresponding to the periodic time of indefinitely small vibrations, and a superior limit equal to the refrangibility of the active light.

234. This theory seems to accord very well with the general character of dispersed beams, as regards the prismatic composition of the light of which they consist. When analysed by a prism, these beams are sometimes found to break off abruptly at their more refrangible border, but I do not recollect ever to have met with an instance in which a beam broke off abruptly at the opposite border, except when the whole beam was almost homogeneous. This is just as it ought to be according to

the above theory, because the amplitude of vibration decreases indefinitely in approaching the less refrangible limit. In the case of a solution of chlorophyll, we may suppose that the part of the molecular forces of restitution depending on first powers of the displacements is considerable, on which supposition, the effect ought to approach to what would take place were there no other part. But were the forces of restitution strictly proportional to the displacements, the vibrations would be isochronous, and could only be excited by ethereal vibrations having almost exactly the same period, but would be powerfully excited by such. Accordingly, in a solution of chlorophyll the dispersion comes on very suddenly; a large part of it is produced by active light of nearly the same refrangibility as the dispersed light; and the latter, by whatever active light produced, has nearly the same refrangibility that it had at first. This supposition, combined with the preceding theory, accounts also for the transparency of the fluid with respect to rays of less refrangibility than the first absorption band, for the great intensity of that band, for the rapidity with which opacity comes on at its less refrangible border, and the comparatively slow resumption of transparency on the other side. A difference of the same nature on opposite sides of a maximum of opacity seems to be a very common phenomenon in absorption. On the other hand, in those numerous cases in which the dispersion comes on gradually, in the manner described in Art. 44, we may suppose the part of the forces of restitution depending on first powers of the displacements to be but small.

235. It may appear at first sight to be a formidable objection to the theory here brought forward, that in the experiment mentioned in Art. 216, the intensity of the dispersed light did not appear to be more than doubled when the intensity of the incident disturbance was doubled; and that in the experiment described in Art. 215, the rays of low refrangibility did not appear to exercise any protecting influence. But the difficulty may, I think, be got over by a very reasonable supposition. It seems very natural to suppose that a given molecule remains for the greater part of the time at rest, or nearly so, and only now and then gets involved in vibrations. On this supposition, it is only a very small per-centage of the molecules that at a given instant are vibrating to an extent worth considering. Conceive now a stream of light consisting of the highly refrangible rays to be incident on a sensitive medium, and to cause 1 per cent. of the sensitive molecules to vibrate considerably, the rest vibrating so little that they may be regarded as at rest. Now imagine a second stream, similar in all respects to the first, to influence the medium which is already under the influence of the first stream. Of the 1 per cent. of the molecules already vibrating, many are vibrating, we may suppose, nearly with their maximum amplitude, and consequently are not much affected. Besides, it is a great chance if the epoch of the ethereal vibrations belonging to the second stream is such as to produce any great tendency either towards quiescence or towards disturbance in a molecule just for the short time that it is vibrating strongly under the influence of the first stream. But of the 99 per cent. of quiescent molecules 1 per cent. are made to

vibrate. Hence the effect of the two streams together is very nearly the same in kind as that of one alone, but double in intensity.

236. The apparent absence of a protecting influence in the less refrangible rays seems at first more difficult to account for, but perhaps the following reasoning may be thought satisfactory. We ought not to attribute more influence in the direction of protection to a second beam of rays of low refrangibility, than in the contrary direction to a second beam of rays of high refrangibility. Now if the effect of a beam of rays of high refrangibility be to throw 1 per cent. of the molecules into a state of vibration, it would be a commensurate effect in a beam of rays of low refrangibility to stop the vibrations of 1 per cent. of the molecules, if they were all vibrating. But since only 1 per cent. are actually vibrating, the real protecting effect amounts to no more than stopping the vibrations of one molecule in every 10,000, an effect which may be regarded as insensible.

237. The simple consideration that work cannot be done without the expenditure of power, shows that when light incident on a medium gives rise to dispersed light, a portion at least of the absorption which the medium is observed to exercise must be due to the production of the dispersed light. If the dispersed light really arises from molecular disturbances, and for my own part I think it almost beyond a question that it does, it follows that in these cases light is absorbed in consequence of its being used up in producing molecular disturbances. But since we must not needlessly multiply the causes of natural phenomena, we are led to attribute the absorption of light in all cases to the production or augmentation of molecular disturbances, unless reason be shown to the contrary. It might seem at first sight that the production or non-production of dispersed light establishes at once a broad distinction between different kinds of absorption. I do not think that much stress can be laid on this distinction. In the first place it may be remarked, that we have no reason to suppose that vibrations which are of the same nature as those of light are confined to the range of refrangibility that the human eye can take in. If, therefore, no dispersed light be perceived, it does not follow that no invisible rays are dispersed. If the incident light belong to the visible part of the spectrum, the dispersed rays (if any), being of lower refrangibility than the incident light, can only be invisible by having a refrangibility less than that of red light, and would manifest themselves solely or mainly by their heating effect. However, though invisible rays of this nature are in all probability emitted by the body in consequence of the absorption of visible light, we are not bound to suppose that in their mode of emission they precisely resemble the visible rays observed in the phenomena of internal dispersion. In most cases, perhaps, they are more nearly analogous to the visible rays emitted by solar phosphori. It is possible to conceive, and it seems probable that there exist, various degrees of molecular connexion from mere casual juxtaposition to the closest chemical union. A compound molecule may vibrate as a whole, by virtue of its connexion with adjacent molecules, or it may vibrate by itself, in the

manner of an isolated vibrating plate or rod, and between these extreme limits we may conceive various intermediate modes of vibration. Hence, without departing from the general supposition that the absorption of light is due to the production of molecular disturbances, we may conceive that the modes in which the ether communicates its vibrations to the molecules, and the molecules in turn communicate their disturbances to the ether, are very various.

I do not bring forward the idea that the absorption of light is due to the production of molecular disturbances as new, though possibly the communication of the ethereal vibrations to the molecules may hitherto have been supposed necessarily to imply the existence of synchronous vibrations among the molecules. The change in the periodic time of vibrations which takes place in the process of internal dispersion would hardly have been suspected, had it not been for the singular phenomenon which pointed it out.

238. The only theory of absorption, so far as I am aware, in which an attempt is made to deduce its laws from a physical cause is that of the Baron Von WREDE, who attributes absorption to interference\*. The Baron's paper is in many respects very beautiful, but it has always appeared to me to be a fatal objection to his theory that it supposes vibrations to be annihilated. It is true that two streams of light may interfere and produce darkness, but then to make up for it more light is produced in other quarters. Light is not lost by interference, but only the illumination differently distributed. Were the disappearance of light in the direction of a pencil admitted into a medium merely a phenomenon of interference, the full quantity of light admitted ought to be forthcoming in side directions. Were a series of vibrations incident on a medium, without producing any progressive change in its state, or any disturbance issuing from it, it would follow that work was continually being annihilated. But we have reason to think that the annihilation of work is no less a physical impossibility than its creation, that is, than perpetual motion.

*List of highly sensitive substances.*

239. For the sake of any one who may wish to make experiments in this subject, I subjoin a list of the more remarkable of the substances which have fallen under my notice. It will be seen that most of these substances were suggested by the papers of Sir DAVID BREWSTER and Sir JOHN HERSCHEL.

Glass coloured by peroxide of uranium: yellow uranite: nitrate or acetate of the peroxide. Probably various other salts of the peroxide would do as well. The absorption bands of the salts, whether sensitive or not, of peroxide of uranium ought to be studied in connexion with the change of refrangibility.

A solution of the green colouring matter of leaves in alcohol. To obtain a solution which will keep, it is well previously to steep the leaves in boiling water. The alcohol should not be left permanently in contact with the leaves, unless it be wished

\* POGGENDORFF'S Annalen, B. xxxiii. S. 353; or TAYLOR'S Scientific Memoirs, vol. i. p. 477.

to observe the changes which in that case take place, but poured off when the strength of the solution is thought sufficient. Also, the solution when out of use must be kept in the dark.

A weak solution of the bark of the horse-chestnut.

A weak solution of sulphate of quinine, *i. e.* a solution of the common disulphate in very weak sulphuric acid. Various other salts of quinine are nearly if not quite as good.

Fluor-spar (a certain green variety).

Red sea-weeds of various shades: a solution of the red colouring matter in cold water. If a solution be desired, a sea-weed must be used which has never been dried. Sometimes even a fresh sea-weed will not answer well.

A solution of the seeds of the *Datura stramonium* in not too strong alcohol.

Various solutions obtained from archil and litmus (see Arts. 65 to 72).

A decoction of madder in a solution of alum.

Paper washed with a pretty strong solution of sulphate of quinine, or with a solution of stramonium seeds, or with tincture of turmeric. The sensibility of the last paper is increased by washing it with a solution of tartaric acid. This paper ought to be kept in the dark.

A solution, not too strong, of guaiacum in alcohol.

Safflower-red, scarlet cloth, substances dyed red with madder, and various other dyed articles in common use.

Many of the solutions here mentioned are mixtures of various compounds. Of course if the sensitive substance can be obtained chemically pure it will be all the better.

#### *Conclusion.*

240. The following are the principal results arrived at in the course of the researches detailed in this paper:—

(1.) In the phenomenon of true internal dispersion the refrangibility of light is changed, incident light of definite refrangibility giving rise to dispersed light of various refrangibilities.

(2.) The refrangibility of the incident light is a superior limit to the refrangibility of the component parts of the dispersed light.

(3.) The colour of light is in general changed by internal dispersion, the new colour always corresponding to the new refrangibility. It is a matter of perfect indifference whether the incident rays belong to the visible or invisible part of the spectrum.

(4.) The nature and intensity of the light dispersed by a solution appear to be strictly independent of the state of polarization of the incident rays. Moreover, whether the incident rays be polarized or unpolarized, the dispersed light offers no traces of polarization. It seems to emanate equally in all directions, as if the fluid were self-luminous.

(5.) The phenomenon of a change of refrangibility proves to be extremely common, especially in the case of organic substances such as those ordinarily met with, in which it is almost always manifested to a greater or less degree.

(6.) It affords peculiar facilities for the study of the invisible rays of the spectrum more refrangible than the violet, and of the absorbing action of media with respect to them.

(7.) It furnishes a new chemical test, of a remarkably searching character, which seems likely to prove of great value in the separation of organic compounds. The test is specially remarkable for this, that it leads to the independent recognition of one or more sensitive substances in a mixture of various compounds, and shows to a great extent, before such substances have been isolated, in what menstrua they are soluble, and with what agents they enter into combination. Unfortunately, these observations for the most part require sunlight.

(8.) The phenomena of internal dispersion oppose fresh difficulties to the supposition of a difference of nature in luminous, chemical, and phosphorogenic rays, but are perfectly conformable to the supposition that the production of light, of chemical changes, and of phosphoric excitement, are merely different effects of the same cause. The phosphorogenic rays of an electric spark, which, as is already known, are intercepted by glass, appear to be nothing more than invisible rays of excessively high refrangibility, which there is no reason for supposing to be of a different nature from rays of light.

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## NOTES ADDED DURING PRINTING.

### Note A. Art. 23.

SHORTLY after the preceding paper was forwarded to the Royal Society, I found M. EDMOND BECQUEREL's map of the fixed lines of the chemical spectrum, which is published in the 40th volume of the 'Bibliothèque Universelle de Genève' (July and August 1842). I had seen in MOIGNO's 'Repertoire d'Optique Moderne,' that the map had been presented to the French Academy, and naturally felt anxious to obtain it; but not finding any further notice of it either in that work or in the 'Comptes Rendus,' I supposed that it had not yet been published. The principal lines in this map I recognized at a glance. M. BECQUEREL's broad band I is my *l*; his group of four lines M with the preceding band forms my group *m*; his group of four lines N forms the first four of my group *n*; his line O is my *n*. It is only in the last group that there can be any doubt as to the identification; but I feel almost certain that M. BECQUEREL's P is my *o*, and the next two lines, the last in his map, are the two between *o* and *p*. It is difficult at first to believe that the strong line *p* should have been left out, while the two faint lines between *o* and *p* are represented, but the difficulty is, I think, removed by considering the feeble photographic action in that part of

the spectrum. M. BECQUEREL expressly states that lines were seen beyond the last he has represented, though they were hardly distinct; and on comparing together his map, Mr. KINGSLEY'S photographs, and my own map, I think hardly any doubt can remain as to the identification.

I take this opportunity of referring to another very interesting paper of M. BECQUEREL'S, entitled 'Des effets produits sur les corps par les rayons solaires,' which is published in the *Annales de Chimie*, tom. ix. (1843) p. 257, with which I was not acquainted till lately, or I should have referred to it before. This paper contains, among other things, an investigation of the effects of transparent and coloured screens on the luminous, chemical, and phosphorogenic rays, in which it is shown, that, notwithstanding the great difference in the action of a given screen on the three classes of rays, when we study the effect of the incident rays as a whole, its action is the very same when we confine our attention to rays of any one refrangibility. Among the media employed by M. BECQUEREL, are some whose absorbing effect I have mentioned in the present paper, as having been determined by methods depending upon the change of refrangibility. In such cases my own results, as might have been anticipated, are in perfect harmony with those of M. BECQUEREL. With respect to the results at which I have arrived regarding the nature of the phosphorogenic rays of an electric spark, which are mentioned towards the end of the paper, I have been in a good measure anticipated by M. BECQUEREL. Yet I do not think that even he was aware that so much of the effect of the spark was due to rays of such high refrangibility.

#### Note B. Art. 105.

I have since succeeded, by a particular arrangement, in seeing so far into the "lavender" rays as to make out the groups of fixed lines *m*, *n*, *p* by means of light received directly into the eye, and even to perceive light beyond that.

As to the colour of these rays when they are well isolated, I think the corolla of the lavender gives as good an idea of it as could be expected from the circumstances. They seem to me to want the luminousness of the blue and the ruddiness of the violet. No doubt much error and uncertainty has hitherto existed both as to the colour and as to the illuminating power of these rays, because the gray prolongation of a spectrum formed on paper by projection has been mistaken for the lavender rays.

#### Note C. Art. 154.

On adding common phosphoric acid to a solution of nitrate of uranium no effect seemed to be produced, but on examining the vessel some days afterwards, a precipitate was found to have fallen. This precipitate proved to be sensitive in a very high degree.

#### Note D. Art. 158.

I have since observed in a mineral solution a system of absorption bands so remarkable, and so closely resembling in many respects those found in the salts of peroxide of uranium, though they occur in a totally different part of the spectrum, that I think no apology is needed for mentioning the circumstance. The medium referred to is a solution of permanganate of potassa, in fact, red solution of mineral chameleon. In order to see the bands, it is essential to employ a dilute solution,



or else to view it in small thickness, since otherwise the whole of the region in which the bands occur is absorbed. The bands are five in number, and are equidistant, or at least very nearly so. The first is situated at about three-fifths of a band-interval above D; the last coincides with F, or, if anything, falls a little short of it. The second and third are the most intense of the set. I have carefully examined the solution for change of refrangibility, and have not found the least trace. Ferrate of potassa shows nothing remarkable.

By means of the bands just mentioned, the colour of permanganate of potassa may be instantly and infallibly distinguished from that of certain other red solutions of manganese, the colour of which some chemists have been disposed to attribute to permanganic acid (see a paper by Mr. PEARSALL 'On red Solutions of Manganese,' Journal of the Royal Institution, New Series, No. IV. p. 49).

Note E. Art. 171.

If we suppose the angle of incidence *exactly* equal to  $45^\circ$ , assume  $\frac{4}{3}$  for the refractive index of the fluid, and apply FRESNEL's formulæ to calculate the ratio of the intensity of light reflected at the exterior surface of a bubble, and polarized in a plane perpendicular to the plane of incidence, to that of light similarly reflected and polarized in that plane, we find 0.228 to 1, a ratio which certainly differs much from one of equality. But in order to render the two intensities equal, it is sufficient to increase the angle of incidence by only  $3^\circ 35'$ ; and in fact, as a matter of convenience, the position of the observer was usually such that the deviation of the light was somewhat greater than  $90^\circ$ , and therefore the angle of incidence somewhat greater than  $45^\circ$ .

Note F. Art. 191.

I have since received a slab of glass of the kind here recommended, which has been executed for me by Mr. DARKER of Lambeth, and which answers its purpose admirably, the medium being eminently sensitive. Besides its general use as a screen, this slab, from its size and form, has enabled me to trace further than I had hitherto done (Arts. 75, 76) the connexion between certain fluctuations of transparency which the medium exhibits and corresponding fluctuations of sensibility.

Note G. Art. 192.

Paper washed with a mere infusion of the bark of the horse-chestnut is quickly discoloured; but a piece washed with a solution which had been purified by chemical means remained white, and proved exceedingly sensitive.

Note H. Art. 204.

I have since ordered a complete train of quartz, of which a considerable portion, comprising among other things two very fine prisms, has been already executed for me by Mr. DARKER. With these I have seen the fixed lines to a distance beyond H more than double that of  $p$ ; so that the length of the spectrum, reckoned from H, was more than double the length of the part previously known from photographic impressions. The light was reflected by the metallic speculum of a SILBERMANN's heliostat, which I have received from M. DUBOSCQ-SOLEIL. With the glass train the group  $p$  was faint, but with the quartz train there was abundance of light to see not only the group  $p$ , but the fixed lines as far as  $Hp1$ , or thereabouts. From the group  $n$  to about the middle of the new region, the lines are less bold and striking than in the region of the groups H,  $l$ ,  $m$ ,  $n$ , but the latter

part of the new region contains many lines remarkable both for their strength and for their arrangement. I hope to make a careful drawing of these lines as shown by the complete train with a summer's sun.

I have some reasons for believing that the photographic action of these highly refrangible rays is feeble, perhaps almost absolutely null. In the second of the papers referred to in Note A. (p. 300), M. BECQUEREL describes an experiment in which a prism of quartz was employed to form a spectrum; and yet the impressed spectrum formed by rays which had traversed the quartz alone was hardly longer than that formed by rays which, in addition to the quartz, had traversed a screen of pure flint-glass a centimetre in thickness. It is possible, I am inclined to think probable, that glass made with *perfectly* pure materials would be transparent like quartz, but all the specimens I have examined were decidedly defective in transparency. Besides, M. BECQUEREL, who may be allowed to be the best judge of his own experiments, considered the result just mentioned as a proof that the impressed spectrum formed by rays which had traversed quartz only did not extend, except a very trifling distance, beyond that formed by his train of glass; and yet his map, formed by means of the latter, does not take in the line *p*.

However, among the multitude of preparations capable of being acted on by light, it is probable that there may be some which are acted on mainly by rays of unusually high refrangibility, and which, on that very account, would not be suitable for the ordinary purposes of photography. With these it is possible that the new region of the solar spectrum might be taken photographically.

#### Note I. Art. 213.

I have since examined the salt, or product, whatever it may be, in the dry state, and under more favourable circumstances, and have found it sensitive, though not by any means in a high degree. It exhibits also the absorption bands which seem to run through the salts of peroxide of uranium.

In connexion with the insensibility of a solution of nitrate of uranium in ether, it seems interesting to mention a fact which I have since observed, namely, that the sensibility of a solution of nitrate of uranium in water is destroyed by the addition of a little alcohol.

#### Note J. Art. 217.

On repeating this experiment on a subsequent occasion, I could not satisfactorily make out the difference of character of a strong and of a weak spark from the prime conductor, perhaps because the machine was in less vigorous action; but the difference between the effects of a mere spark and of the discharge from a Leyden jar was plainly evident. I would here warn the reader, that in order to perform the experiment in such a manner as to obtain a striking and perfectly decisive result, it is essential to employ an excessively weak solution. The reason of this is evident.

A severe thunder-storm which visited Cambridge on the evening of July 16, 1852, afforded me a good opportunity of observing the effect of lightning on a solution of quinine, and other sensitive media. From the copiousness of the dispersed light, it was evident that the proportion of the active, and therefore highly refrangible rays to the visible rays was very far greater in the radiation from lightning than in daylight. A difference of character was observed between the effects of a weak distant flash, and of a bright flash nearly overhead, similar to that which has been described with reference to the effects of a spark from a machine, and of the discharge from a Leyden jar. In

artificial discharges, the stronger the spark the more the rays of excessively high refrangibility seem to abound, in proportion to the whole radiation. Now a flash of lightning is a discharge incomparably stronger than that of a Leyden jar. It might have been expected, therefore, that the radiation from lightning would be found to abound in invisible rays of excessively high refrangibility. Yet I could not make out in a satisfactory manner the absorption of the rays by glass, even by common window-glass. I do not wish to speak positively regarding the result of this observation, for of course observations with lightning are more difficult than those made with a machine which is under the control of the observer. Yet it did seem as if the spark from a Leyden jar was richer than lightning in rays of so high a refrangibility as to be stopped by glass. If this be really true, it must be attributed to one of two things, either the non-production of the rays in the first instance, in the case of lightning, or their absorption by the air or clouds in their passage from the place of the discharge. If they were not produced, that may be attributed to the rarity of the air at the height of the discharge, that is, at the height of the thunder-cloud. No doubt the metallic points of the discharger belonging to the electrical apparatus may have had an influence on the nature of the spark; but I am inclined to think that this influence, so far as it went, would have acted in the wrong direction, that is, would have tended to produce rays of lower, at the expense of those of higher refrangibility.

Note K. Art. 220.

My attention has recently been called to a paper by M. BRÜCKE (*POGGENDORFF'S Annalen*, B. v. (1845) S. 593), in which he describes some experiments which show that the different parts of the eye, and especially the crystalline lens, are far from transparent with respect to the rays of high refrangibility. The eyes employed were those of oxen and some other animals; and the inquiry was carried on by means of the effect which light that had passed through the part of the eye to be examined produced on a film of tincture of guaiacum that had been dried in the dark. Of course the phenomena described in the present paper afford peculiar facilities for such an inquiry, and I had frequently thought of entering upon it, but have not yet made any observations. Independently of the facility of the observations, and the advantage of being able to examine readily light of each degree of refrangibility in particular, the results obtained by means of sensitive media seem to be more trustworthy on this account, that it would be possible to employ fresh eyes. The experiments of M. BRÜCKE necessarily occupied a considerable time, and it may be doubted whether the eye, especially after dissection, might not have changed in the interval, and whether the results so obtained are applicable to the eye as it exists in the living animal.

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