

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 Hk_1 , 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 alkalis. 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 alkalis 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 alkalis. 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° , 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° , 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.