PHILOSOPHICAL TRANSACTIONS.

I. *On the Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver and other Substances, both metallic and non-metallic, and on some Photographic Processes.* *By Sir* JOHN F. W. HERSCHEL, *Bart. K.H. V.P.R.S. &c.*

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1. LEST the title of this communication should induce an expectation of its containing any regular and systematic series of researches developing definite laws, or pointing to any distinct theory of photographic action, it may be as well to commence it by stating its pretensions to be of a much lower kind, its object being simply to place on record a number of insulated facts and observations respecting the relations both of white light and of the differently refrangible rays to various chemical agents, which have offered themselves to my notice in the course of photographic experiments originating in the announcement of M. DAGUERRE's discovery. The facts themselves, in the present state of our knowledge, will, I believe, be found by no means devoid of interest, and may lead, in the hands of others more favourably situated for such researches, and, I may add, in a better climate than ours, to inquiries of the utmost interest.

2. In a communication to this Society, which was read on the 14th of March, 1839, and of which an abstract will be found in the notices of its proceedings for that sitting, I have stated the circumstances which first directed my attention to this subject, and the progress I had then made, both in the scientific part of the inquiry and in its application to the photographic art. As that paper was (at my own request) withdrawn from the further immediate notice of the Society, and as the abstract alluded to may not fall into the hands of those who may read the present communication, a brief recapitulation of its contents will be necessary to preserve the connexion by which my inquiries have been linked together.

3. The principal points of that communication are as follows. 1st. The use of the liquid hyposulphites for fixing the photographic impression, in virtue of the property which they possess (and which was, I believe, first pointed out in my paper on those

salts in Brewster's Edinburgh Philosophical Magazine*) of readily dissolving the chloride and other combinations of silver insoluble in the generality of menstrua. It has since appeared that this is the solvent used by M. Daguerre; and I may add that it is the only one that I have found at once easy of management, and perfectly to be relied on under all circumstances, though there are many which occasionally, or with great attention to nicety of application, succeed well.

4. 2ndly. Observation of the feeble susceptibility of the pure chloride of silver to the action of light, and attempts to attain a greater degree of susceptibility, attempts attended then with very limited and partial success, far surpassed by the curious and powerful processes of Mr. Talbot, not then divulged, as well as by those which I have myself since fallen upon.

5. 3rdly. The application of photography to the copying of drawings and engravings, and to the fixation of optical images. Of course it will be understood that I have no intention here of interfering with Mr. Talbot's just and long-antecedent claims in this or in any other points; but having bestowed much attention both then and since on these processes, so as to produce results far from unsatisfactory, it will be necessary to say a few words in justification of the time and pains I have devoted to this branch of the inquiry.

6. A susceptibility to the action of light, and a power of destroying at any given moment all susceptibility to further action in the ground of a picture, being granted, it obviously depends only on the degree of that susceptibility, and on the precision with which the rays of light can be concentered on or confined to their intended points of action, how far the photographic impression obtained, whether from the camera or the original drawing or engraving to be copied, shall satisfy the wishes of the artist. As regards the camera; that which I employed was neither periscopic nor achromatic, being in fact no other than the aplanatic crown-glass lens computed and described in paragraph 13 of my paper on the aberrations of lenses†. This combination, though admirable for its original purpose as a burning-glass, is in fact one of the worst possible for a photographic camera, in which the three qualities of a flat field, a sharp focus at great inclinations of the visual ray, and a perfect achromaticity, are indispensable. The latter quality, indeed, (as will be apparent enough from the properties about to be described,) is even more necessary for the photographic than for the ordinary use of the camera. In consequence, my first camera pictures were necessarily extremely defective. Nor was I at all anxious on this head, knowing that the other essentials of the photographic problem being secured, the acquisition of a perfect camera would ensure perfection in that respect.

7. A much more important line of inquiry, as far as applications are concerned, appeared to be the exact reproduction of indefinitely multiplied fac-similes of an original photograph once obtained, by which alone the *publication of originals* could be accomplished. And this seemed the more deserving of attention, as it was under-

* Philosophical Transactions, 1821.

† 1819. vol. i. and 1820. vol. ii.

stood that M. DAGUERRE's pictures admitted of no such reproduction, thus giving a decided superiority to the use of paper, or other similar material, provided it could by any means be wrought up to equal perfection of effect.

8. To avoid much circumlocution, it may be allowed me to employ the terms positive and negative, to express respectively, pictures in which the lights and shades are as in nature, or as in the original model, and in which they are the opposite, i. e. light representing shade, and shade light. The terms direct and reversed will also be used to express pictures in which objects appear (as regards right and left) as they do in nature, or in the original, and the contrary. Thus also we may speak of a positive direct, a negative direct, or of a positive reversed or negative reversed picture, to the great saving of words and time. Thus the camera impresses on white paper a negative-reversed photograph. And this being also the character of an engraving transferred on similar white paper, it is evident that a single transfer from a camera picture is equivalent in ultimate effect to a double transfer from an original drawing or from an engraving on such paper.

9. The chief difficulty in the reproduction of drawings or engravings, consists in the necessity of operating a double transfer, so as to produce a resulting impression of the same character as the original in both these respects, whereas from what is above said it appears that this does not apply in the case of a camera picture. Granting therefore that such a picture could be impressed with such depth and sharpness as to be equal in these respects to a finished engraving, the problem of photographic *publication* is solved, since it is a fact that the negative reversed photographic impression of an engraving, however highly finished, such as is obtained by a single transfer on white paper, is quite equal in precision and finish to the original engraving.

10. The above remarks relate only to what may be called the practical part of the photographic art. We come now to points of scientific interest. It is noticed then in the paper above alluded to in abstract, 4thly, That the intensity of chemical action of different rays in the solar spectrum appears to be in great measure disconnected with their colorific impressions on the eye; and this conclusion, generally though unequivocally indicated by a variety of experiments in which coloured glasses were used to analyse and separate the incident rays, will be found confirmed, with many details equally novel and unexpected, in the experiments about to be related, in which the prismatic analysis of the rays has been resorted to.

11. 5thly. A curious property of glass plates in exalting the effect of sunshine on nitrated paper is pointed out; a property of which subsequent experiments have shown the reverse to obtain in certain circumstances, and which the results of these experiments (to be described in the sequel), in place of elucidating, have only served to render more enigmatical.

12. Having no better ground of arrangement under which to group my subsequent experiments, I shall follow this order, so far as it goes, in describing their

principal results, transposing only the second and third heads, so as to keep the scientific part of the subject as distinct as possible from the practical. And first then,

I. *Of fixing Photographs.*

13. As already observed, I find the surest and best fixing material to be a liquid hyposulphite, and of these I prefer that of soda. But in using it some precautions are necessary. The photograph must be first well washed by soaking it in water, to free it from all superabundant nitrate of silver, which is very apt to produce a sulphuret on its first contact with the hyposulphite*. If the paper be prepared with the simple nitrate, the water must be distilled, since the smallest quantity of any muriatic salt present attacks the picture impressed on such paper with singular energy, and speedily obliterates it, unless very dark. A solution containing only a thousandth part of its weight of common salt, suffices to effect this in a few minutes in a picture of considerable strength. But if the paper be already muriated or prepared with other insoluble argentine compounds, this perfect purity of the water is not needed, and a small addition of salt is even beneficial, by removing the silver as fast as abstracted from the paper.

14. This first washing greatly diminishes the sensitiveness of the photograph to further impressions of light, and if merely nitrated, destroys it entirely if the paper be thin. If otherwise, it may be considered as half fixed, and may be preserved, and occasionally inspected in feeble lights, till convenient to fix it completely. To do this it must be thoroughly dried, and then brushed over very quickly with a flat camel-hair brush dipped in a saturated solution of the hyposulphite, first on the face, then on the back. This, having remained on it till the paper is completely penetrated with it, must be washed off with repeated and copious affusions of water, aided by a soft sponge, with a *dabbing* motion, often turning the picture, until the liquid comes off without the slightest *sweetness*. The photograph is then fixed, and may be dried and put by; but to make it quite secure it is best to repeat the process, and if the paper be thick, even a third time.

15. The hyposulphite of soda and silver being liable to spontaneous decomposition, accompanied with separation of silver in the state of sulphuret, it is necessary to be very careful in washing away the very last traces of this salt, especially if it be intended to use the photograph for re-transfers, in which case a deposition of sulphuret within its pores is fatal, since it renders the paper unequally opake. It is for this reason we recommend to apply the hyposulphite concentrated and quickly; since if it be not in excess at every point of the paper, the deposit of sulphuret takes place at the first contact, and can never after be got rid of.

16. Common salt used as a fixing material on paper, when it succeeds, probably acts as a solvent of the chloride or other argentine compound used. At least I find

* See my papers above cited.

that a saturated brine dissolves this substance pretty freely, producing a solution of an intensely bitter metallic taste, from which the greater part, if not the whole chloride, is thrown down by copious addition of water. I cannot say, however, that I have found much satisfaction in the use of salt as a fixing material.

17. Hydriodate of potash, if the right strength be hit, succeeds well; but to do so is not very easy. Moreover, it gives a yellow tint to the ground of the picture, highly unfavourable to transfers. The very curious property possessed by this salt, when applied of a certain strength, of rendering photographic paper, blackened by exposure to light, susceptible of being again whitened by the same agent, has been noticed by LASSAIGNE, Mr. TALBOT and others, and was early encountered by myself. My attempts to apply this property to the production of a *positive* photographic paper, (i. e. a dark ground, on which the action of the light shall impress a *bright* image,) though occasionally successful, and in one or two instances remarkably so, have yet not enabled me to state any precise proportions of ingredients, and mode of applying them, which shall *certainly* produce a paper of the required character possessed of any degree of permanence. In fact, nothing can be more variable and capricious than the results obtained according to the different intensities of the solutions applied—the qualities of the paper—the degree of darkening induced on the paper before the application of the ioduretted solution—the state of the paper as to moisture or dryness, and other circumstances. Nor will this appear strange when the complicated nature of the action itself, when analysed as will be explained in the subsequent part of this paper, is considered. It will there be shown that the total effect of a ray of white light on iodic preparations is in fact the difference of two opposing actions, either of which is susceptible of being exalted or enfeebled at pleasure by circumstances under our command, indeed, in a general way, but difficult to reproduce exactly at our pleasure. When these opposing actions exactly neutralize each other, the paper is insensible. When either preponderates, it is positive or negative in its character according to that of the preponderant action; nay, it may at one and the same moment be positive to light incident under certain circumstances, insensible under others, and negative under a yet different illumination. In reference to practical applications, however, I ought to mention that others appear to have met with better success than I have done, perhaps from operating on a larger scale, in which the proportions of ingredients may be more certainly determined and adhered to. A positive paper of this nature is actually prepared for sale by Mr. ROBERT HUNT of Devonport, specimens of which he has been so obliging as to send me, and which certainly gives results of great promise in this line.

18. A weak solution of ferrocyanate of potash renders argentine papers insensible to light; and as it is readily procured in the shops, which the hyposulphites are not, it would seem to be a very convenient fixing material. Unfortunately, however, it cannot be used for this purpose, since pictures fixed with it, though perfectly insensible to the strongest sunshine, are gradually but very slowly obliterated in the dark.

The disappearance of the darkened portions goes on with remarkable steadiness of progression from week to week and from month to month, till all is gone and the paper reduced to its original whiteness, or (if the ferrocyanate have been used in excess) to a blue colour.

19. By far the most remarkable fixing process with which I am acquainted, however, consists in washing over the picture with a weak solution of corrosive sublimate, and then laying it for a few moments in water. This at once and completely *obliterates* the picture, reducing it to the state of perfectly white paper, on which the nicest examination (if the process be perfectly executed) can detect no trace, and in which it may be used for any other purpose, as drawing, writing, &c., being completely insensible to light. Nevertheless the picture, though invisible, is only dormant, and may be instantly revived in all its force by merely brushing it over with a solution of a neutral hyposulphite, after which however it remains as insensible as before to the action of light. And thus it may be successively obliterated and revived as often as we please. It hardly requires mention that the property in question furnishes a means of painting in mezzotinto, (i. e. of commencing on black paper and working in the lights,) as also a mode of secret writing and a variety of similar applications.

20. The chromate (and probably also the arseniate) of silver is insensible to light, and in certain cases, therefore, where the colour is of little consequence, might be of use as a fixing material.

21. There is a remark which ought not to be omitted in regard to this part of our subject, viz. that it makes a great difference, in respect of the injury done to a photographic picture by the fixing process, whether that picture have been impressed by the long-continued action of a feeble light, or by the quick and vivid one of a bright sun. Even supposing the pictures originally of equal intensity, the half-tints are much less powerfully corroded or washed out in fixing, in the latter case than in the former. It is probable that other atmospheric relations than those which refer to the extinction of the merely luminous rays are concerned in this phenomenon. In an atmosphere so loaded with coal smoke as that of the neighbourhood of London, peculiarities of absorptive action may have place which rarely or never occur elsewhere. The tint of coal smoke is yellow (as may be seen in perfection in a London November fog), and more than one instance of the intense power and capricious singularities of very pale yellow media in their action on the chemical rays will come hereafter under our notice. In the locality from which this paper is dated, a light easterly wind brings with it abundant smoky haze from London, to which rural prejudices assign the name of "blight" and attribute an insect origin. On such occasions, when the sky has been otherwise cloudless, (comprising nearly half the poor allowance of sunshine of the last summer,) I have been continually at once annoyed and surprised, by the slowness of photographic action, and by the fugitive nature of its results under the process of fixing.

II. *Of taking Photographic copies and transfers.*

22. I shall not long detain the Society with an account of the various trials I have made for perfecting the multiplication of photographs. The following are the chief precautions it will be generally found necessary to attend to.

23. *First.* An extremely close contact of the photographic paper with the original to be copied, which can only be ensured by subjecting both (laid face upon face) to the pressure of powerful screw-clamps acting on plates of very thick glass. The largest pictures I have copied occupied 110 square inches of exposed surface (eleven inches by ten), and for these dimensions a thickness of glass equal to the one third of an inch was found barely sufficient, or rather too weak. This thickness is, however, ample for photographs whose dimensions do not exceed fifty or sixty square inches. The glass should of course be as colourless as possible, and rather verging to a blue than a yellow or pink tint, yellow media being especially active in absorbing the chemical rays, as will hereafter be shown. The glass should press the papers on some soft bed, such as velvet, stretched on a thick board of a truely plane surface. The contact should be as close as can be produced by any pressure short of what will break the glass, as the smallest interval is injurious by allowing dispersed light to spread. Even that arising from the interposition of a thin film of mica is hurtful to the sharpness of the impression.

24. When only a single transfer is to be made, closeness of contact is the only precaution to be attended to; and this being taken, the transfer takes place with perfect fidelity, and with a depth and sharpness fully equal to the original. But if the photograph so obtained be used for making a re-transfer, a host of annoyances and difficulties arise from the imperfections and unequal and uncertain texture of the paper, as well as from the subtle nature and want of absolute opacity in the reduced silver deposited under the influence of the light, and in which the design is traced, to which must be added the great care which must be bestowed on the fixing process and final washing out of every particle of silver except what actually enters into the design, and which is by no means easy if any but very thin paper be used.

25. Such paper is easily procured of very even texture, but if examined in the light it is found penetrated with actual *holes*, which though of minute dimensions, suffer light to pass freely and are very injurious. To obviate this, and to equalize the light by dispersion, an additional thickness of such paper may be advantageously interposed between the glass and the photograph to be re-transferred. And, finding this in fact to be quite necessary to the production of a tolerably good effect, it occurred to me to impress this paper also with a facsimile of the original, or in other words to double the photograph intended to be re-transferred. This may be done by taking off two such photographs from the original design, which being fixed, dried and pressed flat, are to be applied to each other (face to back), and being first delicately adjusted under a magnifier, by fiducial points made with a fine needle in each, are in

that position to be cemented together at the edges, or rather at four points, one in the middle of each side. The operation is easier than it would appear to be by the description, and the resulting effect offers an infinitely nearer approach to that of an ordinary copper-plate engraving or mezzotinto, than anything that can be got from a single model.

III. *Of the Preparation of Photographic Paper.*

26. It would be tedious and serve little purpose, were I to recite individually the numberless combinations I have tried with a view to the increase of sensitiveness and facility of preparation of this useful material; especially as, after all my trials, I am obliged to admit (which I most readily do) that the specimens recently placed in my hands by Mr. TALBOT far surpass in respect of sensitiveness any that I have yet produced of a manageable kind, and that for all ordinary purposes I have ended in adopting his process of preparation, as far as I understand it. Nevertheless, as all my earlier inquiries were conducted in ignorance of these processes, and as they have led to some results worth notice even in this line, I shall set down a few particulars.

27. My first attention was directed to the discovery of a liquid, or emulsion, which by a single application, whether by dipping or brushing over, should communicate the desired quality. The presence of organic matter having been considered by some late chemists an essential condition for the blackening of the nitrate of silver, I was induced to try in the first instance a variety of mixtures of such organic soluble compounds as would not precipitate that salt. Failing of any marked success in this line, (with the somewhat problematic exception of the gallic acid and its compounds,) the next idea which occurred was that of introducing organized salts of silver into the pores of paper, by first washing it over with an organic, soluble, precipitable salt, with alkaline base, and then with nitrate of silver. Here also, no distinct result was obtained, except that when the uric acid and alkaline urates* were employed, a paper was obtained decidedly more sensitive than that resulting from the nitrate alone, but which blackened spontaneously in the dark.

28. A great many experiments were made by precipitating organic liquids, both vegetable and animal, with solutions of lead, as also, after adding alum, with alkaline solutions. Both alumina and oxide of lead are well known to have an affinity to many of those fugitive organic compounds which cannot be concentrated by evaporation without injury; an affinity sufficient to carry them down in combination, when precipitated either as hydrates or as insoluble salts. Such precipitates when collected were applied in the state of cream on paper, and when dry were washed with the nitrate. It was here that the first prominently successful result was obtained. The precipitate thrown down from a liquid of this description by lead was found to give a far higher degree of sensitiveness than any I had before obtained; receiving an equal depth of impression, when exposed, in comparison with mere

* From the *Boa Constrictor*. My specimen had been long kept, at least fifteen years.

nitrated paper, in less than a fifth of the time, and moreover acquiring a beautiful ruddy-brown tint almost amounting to crimson, with a peculiarly rich and velvety effect.

29. Alumina, similarly precipitated from the same liquid, gave no such result. Struck by this difference, which manifestly referred itself to the *precipitant,* it now occurred to me to omit the organic matter, (whose necessity I had never before thought of questioning,) and to operate with an alkaline precipitant on a mere aqueous solution of nitrate of lead, so as to produce simply a hydrate of that metal. The result was instructive. A cream of this hydrate, being applied and dried, acquired, when washed with nitrate of silver, a considerable increase of sensitiveness over what the nitrate alone would have given, though less than in the experiment where organized matter was present. The rich crimson hue also, acquired in that case under the action of the light, was not now produced. Two peculiarities of action were thus brought into view; the one, that of the oxide of lead as a *mordant,* (if we may use a term borrowed from the art of dyeing,) the other, that of the organic matter as a colorific agent. The former action, as more immediately interesting, claimed the first attention, and the more so, on account of the analogy which it seemed to offer with a similar *mordant* action of the chloride of silver itself, in Mr. TALBOT's curious process of successive alternate washes with salt and nitrate of silver, which by this time had been divulged by him. Of this action, the observed effect seemed to promise an explanation, should it be found to occur when other metallic oxides were substituted for lead, or other salts of this metal for the hydrate.

30. Paper washed with acetate of lead was therefore impregnated with various insoluble salts of that metal, such as the sulphate, phosphate, muriate, hydriodate, borate, oxalate, and others, by washing with their appropriate neutral salts, and when dry, applying the nitrate of silver, as usual. The results, however, were in no way striking as respects sensitiveness, in any case but in that of the muriatic applications. In all cases where such applications were used, a paper was produced infinitely more sensitive than any I had at that time made. And I may here observe that, in this respect, the muriate of strontia appeared to have decided advantage. I should observe that up to this time I had purposely abstained from repeating Mr. TALBOT's experiment above alluded to, being desirous of seeing what progress I could make in the inquiry without external aid. Comparative trials now made with some specimens of his preparing, satisfied me that in point of sensitiveness the two papers (with *mordant bases* of lead and silver) were nearly on a par*. In consequence of this I continued for some

* This does not refer to the later improvements made by Mr. TALBOT in the preparation of his paper, whether by the use of the bromurets or other means yet undescribed by him. I have already alluded to the exquisite sensitiveness of some specimens he has been obliging enough to send to me. It may be right to mention the date of the experiments described in (29.) and (30.) of the text, which are respectively April 19 and 27, 1839.

time to use (and at the time much to my satisfaction) my own process* in the preparations of paper for the copying of designs, as well as for the camera. By degrees, however, an inconvenience, little expected, appeared. The paper with a basis of lead turns yellow by keeping in the dark, and the tint goes on gradually deepening to a dark brown. But, what is very singular, this change is not equally rapid in all kinds of paper, a difference depending no doubt on the size employed, which, it may be observed here once for all, is of the utmost influence in all photographic processes. In one sort of paper (known by the name of *blue wove post*) it is instantaneous, taking place the moment the nitrate (if abundant) is applied. And yet I find this very paper to resist discoloration, by keeping, better than any other, when the mordant base is silver in place of lead. On the other hand, a paper of that kind called *smooth demy*, rendered sensitive by the process described in (28.), was found to acquire, by long keeping, a grey or slate colour, which increases to such a degree as might be supposed to render it useless. Yet in this state, when it is impressed with a photographic image, the process of fixing with hyposulphite of soda destroys this colour completely, leaving the ground as white as when fresh prepared. This fortunate restoration, however, does not take place when the paper has been *browned* as above described. Some of the muriatic salts also are more apt to induce this discoloration than others, especially those with earthy bases. But the effects in this respect are so capricious, that it is vain to attempt giving any connected account of them.

31. In consequence of this spontaneous discoloration†, I disused, for ordinary purposes, this mode of preparation, and adopted the following series of washes, on Mr. Talbot's principle, viz. 1st, nitrate of silver, S. G. = 1·096 (say 1·1); 2ndly, muriate of soda, 1 salt + 19 water; 3rdly, nitrate of silver, S. G. 1·132 (say 1·15), saturating the muriatic solution with chloride of silver, and occasionally dividing the last application into two consecutive washes of equal strength by dilution. This, as an ordinary working paper, is easily prepared, and has sensibility enough for most purposes. It gives very good camera pictures, and, if that particular sort of paper above named be used, it retains its whiteness well in the dark, at least for some weeks.

32. Paper of this kind may not always be at hand, nor under the same name may the same quality be always depended on, and every other sort I have tried discolours under this preparation, though much more slowly than when lead is used. Being much annoyed with this, I adopted for camera pictures a process which proved both convenient and effectual, and which applies equally well to both descriptions of

* 1st, or mordant wash, saturated solution of acetate of lead.

2nd, weak solution of common salt, containing $\frac{1}{20}$ of salt.

3rd, nitrate of silver, S. G. = 1·20, which however is best applied in two consecutive washes each of S. G. 1·10.

† Some camera pictures which I carried with me to Paris, and which were prepared on the 28th of April, were found on arrival much discoloured; and others prepared at the same time, were turned brown on my return from France about a month afterwards. (Neither had been fixed.)

paper. It consists in simply delaying the last or efficient wash of nitrate of silver, on which the sensitive quality depends, till the moment of using it, and in fact using the paper actually wet with the nitrate, and applied with its sensitive face against a glass plate whose hinder surface is in the focus of the camera. This affords other collateral advantages: 1st, that all crumpling or undulation of the paper is avoided; 2nd, that, being rendered in some degree transparent, the light is enabled to act deeper within its substance. If lead be used as the mordant basis of the paper, it is manifest that it can sustain no injury whatever by keeping or exposure, there being no ingredient on which the light can act, present, until the moment it is used*.

33. My attempts to generalize the property of lead above described, of acting as a mordant, have proved unsuccessful. Those metals only could be practically useful which give white combinations (*leucolytes*). Of these I found that paper impregnated with hydrate of bismuth, by wetting it with the nitrate of that metal and then soaking in water (by which it acquires a beautiful whiteness) comports itself as ordinary paper. The insoluble salts of mercury, even calomel, are also without effect, as indeed are many of those of silver itself, as the sulphate, borate, &c. I mean without effect in giving a high degree of sensibility; for in other respects they are far from inefficacious, as will presently appear.

34. It frequently happens that however carefully the successive washes are applied, so as apparently to drench completely every part of the paper, irregular patches in the resulting sheet will be of a comparatively much lower degree of sensibility, which degree is nevertheless uniform over their whole area. These patches are always sharply defined and terminated by *rounded* outlines, indicating as their proximate cause, the spreading of the wash last applied within the pores of the paper. They have been noticed and well described by Mr. TALBOT, and ascribed by him, I think justly, to the assumption of definite and different chemical states of the silver within and without their area, which it would be highly interesting to follow out. They are very troublesome in practice, but may be materially diminished in frequency, if not avoided altogether, by saturating the saline washes used, previous to their application, with chloride of silver (see § 16.). By attending to this precaution, and by dividing the last wash of the nitrate into two of half the strength applied one after the other, drying the paper between them, as recommended in Art. 30, Note, their occurrence may be almost entirely obviated.

35. With a view to ascertain how far organic matter is indispensable to the rapid discoloration of argentine compounds, a process was tried which it may not be amiss to relate, as it issued in a new and very pretty variety of the photographic art. A solution of salt of extreme dilution was mixed with nitrate of silver, so dilute as to form a liquid only slightly milky. This was poured into a somewhat deep vessel, at the bottom of which lay horizontally a very clean glass plate. After many days, the

* Mr. TALBOT, to whom I communicated this process, wrote me word in reply, that he also had been led by his own experience to adopt a manipulation of the same kind though somewhat different in detail.

greater part of the liquid was decanted off with a siphon tube, and the last portions very slowly and cautiously drained away, drop by drop, by a siphon composed of a few fibres of hemp, laid parallel and moistened without twisting. The glass was not moved till quite dry, and was found coated with a pretty uniform film of chloride of silver, of delicate tenuity and chemical purity, which adhered with considerable force, and was very little sensible to light. On dropping on it a solution of nitrate of silver, however, and spreading it over by inclining the plate to and fro, (which it bore without disturbing the film of chloride,) it became highly sensitive, although no organic matter could have been introduced with the nitrate, which was quite pure, nor could any indeed have been present, unless it be supposed to have emanated from the hempen filaments which were barely in contact with the edge of the glass, and which were constantly *abstracting* matter from its surface in place of introducing new.

36. Exposed in this state to the focus of a camera, with the glass towards the incident light, it became impressed with a remarkably well-defined negative picture, which was direct or reversed according as looked at from the front or the back. On pouring over this, cautiously by means of a pipette, a solution of hyposulphite of soda, the picture disappeared, but this was only while wet, for on washing in pure water and drying, it was restored, and assumed much the air of a Daguerrotype when laid on a black ground, and still more so when smoked at the back, the silvered portions reflecting most light, so that its character had, in fact, changed from negative to positive. From such a picture (of course before smoking) I have found it practicable to take photographic copies; and although I did not, in fact, succeed in attempting to thicken the film of silver, by connecting it, under a weak solution of that metal, with the reducing pole of a voltaic pile, the attempt afforded distinct indications of its practicability with patience and perseverance, as here and there, over some small portions of the surface, the lights had assumed a full metallic brilliancy under this process. I would only mention further to those who may think this experiment worth repeating, that all my attempts to secure a good result by *drying* the nitrate on the film of chloride have failed, the crystallization of the salt disturbing the uniformity of the coating. To obtain delicate pictures, the plate must be exposed wet, and when withdrawn must immediately be plunged into water. The nitrate being thus abstracted, the plate may then be dried, in which state it is half-fixed, and is then ready for the hyposulphite. Such details of manipulation may appear minute, but they cannot be dispensed with in practice, and cost a great deal of time and trouble to discover.

37. This mode of coating glass with films of precipitated argentine or other compounds, affords, it may be observed, the *only* effectual means of studying their habitudes on exposure to light, free from the powerful and ever-varying influence of the *size* in paper, and other materials used in its manufacture, and estimating their degree of sensibility and other particulars of their deportment under the influence of reagents. I find, for example, that glass so coated with the iodide of silver is much

more sensitive than if similarly covered with the chloride, and that if both be washed with one and the same solution of nitrate, there is no comparison in respect of this valuable quality, the iodide being far superior, and of course to be adopted in preference for the use of the camera. It is however more difficult to fix, the action of the hyposulphites on this compound of silver being comparatively slow and feeble.

38. When the glass is coated with bromide of silver, the action, *per se*, is very slow, and the discoloration ultimately produced far short of blackness; but when moistened with nitrate of silver, S. G. 1·1, it is still more rapid than in the case of the iodide, turning quite black in the course of a very few seconds' exposure to sunshine. Plates of glass thus coated may be easily preserved for the use of the camera, and have the advantage of being ready at a moment's notice, requiring nothing but a wash over with the nitrate, which may be delayed till the image is actually thrown on the plate and adjusted to the correct focus with all deliberation. The sensitive wash being then applied with a soft flat camel-hair brush, the box may be closed and the picture impressed, after which it requires only to be thrown into water and dried in the dark to be rendered comparatively insensible, and may be finally fixed with hyposulphite of soda, which must be applied hot, its solvent power on the bromide being even less than on the iodide.

39. Analogous to the chloride, iodide, and bromide of silver, is the fluoride. I have not experimented on it, but should it be decomposed by light, either *per se*, or aided by the nitrate, it seems extremely probable that the nascent fluorine or hydrofluoric acid disengaged, finding itself in contact with glass, might corrode it, and thus produce *an etching*, a result well worth some trouble to obtain.

40. Of organic salts of silver precipitated on glass, I have tried several. The results are very widely different from those obtained by washing over papers, and will form a separate subject of study. Some of them (as the oxalate) form very even and most delicate coatings, highly sensible to light, and, what is remarkable, differing greatly in this respect according as the side next the glass, or that in contact with air, is exposed to it.

41. Light has long been known to reduce the salts of gold as well as silver, and I have shown* that platina in some of its combinations is also very powerfully affected by the same agent. From the use of these metals it was reasonable to look for results of an interesting nature. It might, for instance, be expected that by applying the chloride of one or other of them as a ground or mordant for the reception of a wash of an argentine solution, the reduction of both the silver and the mordant metal would take place, and thus a more rapid and intense blackening would be produced than in the case of silver alone. The well-known instability of the oxide of gold under deoxidizing influences generally, and the intense colouring power of this metal would, *à priori*, render it probable that cases of unstable equilibrium might occur, which the action of a very feeble light might overset.

* See London and Edinburgh Philosophical Magazine, New Series, No. 1, 1832.

42. Papers were washed with the chlorides of gold and of platina, freed from excess of acid. In the case of platina, they proved insensible; in that of gold, a slow but regularly increasing darkening takes place, and the paper at length, under the influence of light, becomes purple. A wash of nitrate of silver increases, but not to a high degree, the sensibility of the aurated paper, but that impregnated with platina remains insensible, unless the nitrate be in great abundance.

43. In the chlorides both of gold and platina, nitrate of silver produces precipitates. In that of gold, the precipitate is of a yellow-brown colour, and in that of platina, a pale yellow. Both are possibly metallic double salts in which the gold or platina, as well as the silver, is in the state of chloride. As relates to the action of light, I find the precipitate of gold very little sensitive if spread on glass, that of platina not at all. On paper, the aurated precipitate is blackened somewhat more readily.

44. If paper impregnated with oxalate of ammonia be washed with chloride of gold it becomes, if certain proportions be hit, pretty sensitive to light; passing rather rapidly to a violet purple in the sun. It is next to impossible to dry paper so prepared, however, as a very gentle heat blackens it. It passes also to the same purple hue in the dark, though much more slowly; so that, as a photographic combination, it is useless.

45. Paper impregnated with acetate of lead, when washed with perfectly neutral chloride of gold, acquires a brownish yellow hue and a sensibility to light which, though not great, is attended with some peculiarities highly worthy of notice. The first impression of the light seems rather to whiten than to darken the paper, by discharging the original colour, and substituting for it a pale greyish tint, which by slow degrees increases to a dark slate colour. But if arrested while yet not more than a moderate ash-grey, and held in a current of *steam*, the colour of the part acted on by light (and of that only) darkens immediately to a deep purple. The same effect is produced by immersing it in boiling distilled water. If plunged in cold water the same change comes on more slowly, and is not complete till the paper is dried by heat. A *dry heat* however does not operate this singular change. The best way of making this and similar experiments is to shade one half the paper operated on with an opake screen closely applied, and to reserve portions, before and after exposure, for comparison.

46. This is not the only case in which the impression made by light is rendered more evident by subsequent applications. A solution of chloride of platina in ether being washed over a bibulous paper impregnated with hydriodate of potash, in certain degrees of strength and copiousness, browns pretty rapidly in the dark, but much more rapidly and to a much deeper tint in sunshine. A paper so washed and partly shaded, on exposure produced a well-defined figure of the shading body, which, on the addition of a fresh wash of the hydriodate, *out of the light*, became much more strongly contrasted with the surrounding ground.

47. Paper (No. 644) washed with acetate of lead and then with chloride of platina, is absolutely insensible, and only becomes very feebly sensible when thoroughly

impregnated with nitrate of silver. But if, in place of the nitrate of silver, a wash of hydriodate of potash be superadded, the effect is remarkable. If the hydriodic solution be strong and plentiful, the paper is immediately coloured dark brown, whether in light or darkness. If very weak, no effect; but if applied of a certain intermediate strength, though not *immediately* affected in the shade, yet, if held (while wet) in the sun, it darkens with extraordinary rapidity to the same deep brown hue, *and presently after, the exposure to the sun continuing, whitens again.* A fresh dose of the hydriodate being applied, it again darkens, but is no longer capable of restoration, and the darkness then goes on increasing to a fine deep chocolate brown. The paper with which I have found this experiment to succeed best is called "smooth wove demy." It requires a clear and steady sun. If gold be substituted for platina, the hydriodic salt exercises, in virtue of its ordinary chemical relations, so powerful a darkening effect, that the influence of light can hardly be traced; but, as far as can be ascertained, something of the same sort obtains here also.

48. In the experiment of the last article we see that the influence of the hydriodic salt, contrary to its usual habitudes (see Art. 17), is to exalt the deoxidizing action of the light, and even to call that action into evidence where it either did not exist, or was masked before. This is not, however, by any means a singular instance. Hydriodate of potash, when very weak, acts in combination with nitrate of silver to produce a paper much more sensitive than the nitrate alone, the remarkable peculiarities of which will be noticed further on. A paper endowed with a pretty high degree of sensibility may also be prepared with the following triple application, viz. 1st, Acetate of lead; 2nd, Hydriodate of potash; 3rd, Nitrate of silver. And here also a phenomenon, something of the same kind as was described in the subsequent part of the experiment of the last article, occurs; for if paper so prepared and darkened in the sun be washed over with a fresh dose of the hydriodate, the exposure to sunshine being continued, it whitens with great rapidity*; and were it practicable (which I have not found it) to ensure precisely the same ingredient-proportions and the same degree of blackening in the sun to start from, I should not hesitate to propose this as an excellent process for a *positive* photographic paper*. A still more remarkable example of the power of this salt to stimulate the *darkening* action of the sun's rays, is to be found in its combination with the tartrate of silver. But of this more hereafter, when we have become better acquainted with the separate action of the different elementary rays, which it is necessary to study before we can understand the complex relations which enter into these phenomena. To this therefore I hasten.

IV. *Chemical Analysis of the Solar Spectrum.*

49. That rays of different colours and refrangibilities have not all an equally energetic action in effecting chemical changes, has long been understood; and that the

* Another paper which possesses this property in an eminent degree is prepared with 1st, acetate of lead; 2nd, sulphate of soda; 3rd, nitrate of silver, darkened in the sun and washed with the hydriodate.

most energetic in the reduction of argentine compounds are those which have been hitherto regarded as extra-spectral, or as lying beyond all visible illumination on the more refrangible side, is a proposition familiar to photologists. How far this opinion is strictly correct I shall take occasion presently to examine. It has also, on the ground of Dr. WOLLASTON's experiments on guaiacum, been received, that the less refrangible end of the spectrum produces chemical changes of a certain kind; but as that eminent philosopher found changes apparently of the same kind, in that substance, to be operated by a gentle heat, unaccompanied with light, and as those changes were, in consequence, referred by him to the calorific rays, which we know to accompany that end of the spectrum, rather than to any peculiar chemical action, this point must be considered as hitherto undecided. The facts about to be stated, however, leave no further doubt on the subject.

50. The experiments described in my first communication on this subject, in which coloured and other media were used to analyse the incident light by absorption, are quite sufficient to show a high probability at least that the chemical energy is distributed throughout the spectrum in such a way as to be, by no means, a mere function of the refrangibility, but to stand in relation to other physical qualities, both of the ray and of the analysing medium, and *that* relation by no means the same as that which determines the absorptive action of the latter on the colorific rays. The experiments I am about to describe will show that there is also a third set of relations concerned in this action, and most materially influencing both the amount and character of the chemical action at each point of the spectrum, viz. those depending on the physical qualities of the substance on which the rays are received, and whose changes indicate and measure their action. This indeed might be expected, or rather it would seem unlikely, on a general view, that the contrary should be true, seeing that some substances are, others are not, affected by light. But no such general and *à priori* reasonings would, I think, lead us to many of the conclusions actually arrived at; as, for instance, that one and the same spectrum thrown on papers differently prepared, shall indicate by the impressions photographically left on those papers, the most capricious differences in the *scale of action*, whether estimated by the extent of the discoloration in the direction of the length of the spectrum, or by its intensity at different points of that length. We could hardly have predicted, *à priori*, for example, that, acting on one description of paper, the chemical spectrum (as indicated merely by the length of its photographic impression,) should include within its limits the *whole* luminous spectrum, extending much beyond the extremest visible red rays on the one hand, and on the other to a surprising distance beyond the violet; while, if another paper be used, all action should appear definitively cut off at the orange; if another, at the commencement of the green; and if another, at that of the blue rays: *that*, in the case of one description of paper, the maximum of apparent action should lie *beyond*, in that of another *within* the visible violet; in a third far in upon the blue; while in a fourth several successive maxima should appear. Still less would any

à priori conclusion prepare us for differences in the *kind* of action at different points of the spectrum, as manifested by differences of colour produced, or for what at first sight appears yet more singular, the *shifting upon the spectrum itself* of the points where these differences of action commence and terminate. Nor, lastly, could any penetration enable us to anticipate a fact so totally at variance with all our ideas, as that two rays of different refrangibilities, (and therefore of different lengths of undulation) acting at once, should produce an effect which neither of them acting separately is competent to produce at all; a fact which seems difficult to deal with on any theory of light. These are but a few of the many singular results which promise to render this field of research, hardly yet entered upon, as replete with novelty, variety, and interest, as any other department in the vast field of physical optics.

51. My first experiments on this subject were directed to the detection of inactive spaces (if any) in the chemical spectrum, analogous to the dark lines of WOLLASTON and FRAUNHOFER in the luminous one. Possessing at the time no means of fixing a sunbeam of large area, I operated coarsely with a prism placed horizontally. The light was introduced through a narrow slit, and the time chosen for experiment when the sun was on the meridian, so that no motion of the spectrum in the direction of its length might confound the result. This arrangement proved, as indeed I expected, quite inadequate to the end proposed; but it sufficed to reveal several leading facts, viz. 1st, That with the paper employed (which happened to be a specimen prepared by the process in art. 31. on Mr. TALBOT's principle) the maximum of action was not beyond the violet, as I had always understood it to be, but rather about the confines of the blue and green, nearly where FRAUNHOFER's ray F is situated. 2ndly, That the extent of the chemical spectrum beyond the visible violet light far surpassed any idea I had previously formed of it. For, in fact, the visible termination of the violet rays nearly bisected the photographic image impressed on the paper. 3rdly, That *in* the visible violet rays there occurred a sort of minimum of action, about one third of the way from FRAUNHOFER's ray H towards G. 4thly, That the whole of the red, up to about FRAUNHOFER's line C, appeared to be inactive. And 5thly, That where the orange-red rays, or the less refrangible half of the portion from C to D in FRAUNHOFER's spectrum, fell, there was communicated to the paper a sort of ruddy tint, a dull brick red.

52. From this experiment, coarsely performed as it was, several practical conclusions came to be deduced. 1st, The absolute necessity of an achromaticity in the object-lens of a photographic camera, of a very perfect kind, and in some sort *sui generis**, is rendered evident by the great extension of the chemical spectrum. And it is equally clear that this very extension affords the most perfect and certain means

* A lens photographically perfect, or which unites all the chemical rays into one focus, may be called *amacratic* (*αμα together, κρατος power*) or *amasthenic* (*σθενος force*). If this nomenclature be adopted, a *diacratic* or diasthenic medium will be one which transmits the chemical power or force; *diacratescence* that quality in virtue of which it does so, &c. &c. In place of the awkward word *diathemaneity*, however, I would venture to propose its Latin version, *transcalescence*.

of testing the perfection actually attained in this respect. Neither the refractive nor dispersive indices best adapted for an ordinary double achromatic lens are exactly those most fitted to collect the chemical spectrum. To determine those which are so, the method pointed out in my Treatise on Light* seems, on the whole, best adapted, viz. by over correcting the crown lens, by a flint one somewhat too concave, and then separating the lenses, till it is found on trial that the adjustment is complete. The dispersive ratio best adapted to the purpose will then be found by the formula there stated. For the refractive indices, those corresponding to FRAUNHOFER's ray F will probably suffice.

53. Another and highly important practical conclusion which seems to be pointed to by this experiment, is the possible future production of naturally coloured photographic images. The feeble traces of colorific power above noticed might become exalted by the use of other combinations, which it therefore became extremely interesting to vary in every possible way. Mr. TALBOT has already observed, that in copying, photographically, designs on coloured glass, the *red* portions would *occasionally* impart a corresponding tint to the impression of that particular portion of the design so coloured. The *rationale* of this fact, as will afterwards appear, is somewhat more complex than it would seem to be on perusing the experiment just cited. The bright red varieties of coloured glass by no means transmit the red rays in a state of purity; and those varieties which do so or nearly so, are incapable of producing the effect in question, if the paper be fresh prepared and completely free from all traces of previous photographic action. At the moment, however, the direct explanation seemed satisfactory, and proved an incentive to further inquiry.

54. July 9, 1839.—A highly concentrated spectrum was therefore formed, by receiving the rays after emergence from the prism used in the last-described experiment

1. Colours of the luminous spectrum.	2. Colours impressed on the paper.
Extreme red†	None.
Mean red	None.
Orange	Faint brick-red.
Orange-yellow	Brick-red, pretty strong.
Yellow	Undecided; red passing into green.
Yellow-green	Dull bottle-green.
Green	Dull bottle-green, passing into blueish.
Blue-green	Very sombre blue, almost black.
Blue	Black, but when the exposure was long continued, metallic yellow, like an imperfect gilding.
Violet	Black, passing into the same metallic yellow by long exposure in the less refrangible portions of the violet ray.
Beyond the violet	Violet-black, or purplish-black.

* Encyclopædia Metropolitana, art. LIGHT.

† As in this table I use for the first time in this paper the expression "extreme red," it will be well to define what is meant here and in the sequel by that term. The extreme red rays intended, then, are those which are brought into view by defending the eye while looking at the spectrum with one or more thicknesses of that sort of deep blue glass which is common enough in commerce, and which I am told owes its colour to smalt,

(a beautiful crown-glass prism by FRAUNHOFER), on a large crown lens, and receiving the focus on paper prepared as in Art. 31. The result was equally striking and unexpected. A very intense photographic impression of the spectrum was rapidly formed, which, when withdrawn and viewed in moderate daylight, was found to be coloured with sombre, but unequivocal tints, imitating those of the spectrum itself. These tints were as stated in column 2 of the preceding Table, the colours at the corresponding points of the luminous spectrum being those in column 1.

I have not succeeded in fixing these tints. They are, however, susceptible of half-fixing by the mere action of water, and may be viewed at leisure in moderate daylight, or by candlelight. And what is not a little remarkable, instead of fading, by keeping in the dark, they become much more evident and decided after a few days. And this, I would observe once for all, is a phenomenon of constant occurrence, whatever be the preparation of the paper used, i. e. when colours are produced at all.

55. The metallic yellow, induced by the blue and least refrangible violet rays, seems to mark the extreme action of the solar light on this particular preparation of paper, and perhaps on one or two other sorts, by the formation of a pellicle of metallic silver thick enough to reflect light with some degree of copiousness. Accordingly, this pellicle is apt to appear as a *bright* border or framing round the photographic copies of engravings, where not covered by the original, and when long exposed, and, in some cases, even in the strong lights of the pictures themselves.

Extension of the visible Prismatic Spectrum.—A new Prismatic Colour.

56. A variation in the experiment of Art. 54. deserves to be described, not so much on account of its bringing into view any photographic novelty, as for its confirming and placing in distinct evidence a fact which I have long more than suspected, but have always hitherto hesitated to announce. The fact to which I allude is that of the existence of *luminous* rays beyond the violet, but not affecting the eye with a sensation of violet, nor of any other of the recognised prismatic hues, but rather with that colour which is commonly termed lavender-grey; at least such is the impression

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i. e. to cobalt. This glass insulates two red rays of definite refrangibilities; one which I call the mean red, the other the extreme red. This latter is situated so decidedly at the extremity of the visible spectrum, that if a dot be made in the centre of the well-defined and round solar image to which it corresponds, and the glass be then laid aside, that dot is judged by the eye to lie exactly at the end, or if anything rather beyond than within the end of the visible spectrum. This is the ray which forms the subject of a communication to the Royal Society by Mr. COOPER (read May 16, 1839), but which I have pointed out to the especial notice of photologists on several occasions, viz. 1st, in my paper on the action of crystallized media on homogeneous light, read December 23, 1819, and printed in the Philosophical Transactions for 1820 (See vol. cx. p. 88); 2ndly, in a paper read November 18, 1822, before the Royal Society of Edinburgh, and printed in the Transactions of that Society for 1822; 3rdly, in my Treatise on Light (Encyclop. Metropol. §§ 487, 497, 503.). This ray has, in fact, been constantly used and recommended by me as a standard ray, for which purpose it is admirably adapted on account of the facility of insulating it in a state of purity.

they produce on my own eye, as well as on that of a friend to whom I have shown them, and who proposed that term, or that of simple grey, to express it. It was in the course of my experiments on the polarized rings in 1819, made with M. BIOT's apparatus, that I was first led to something approaching to conviction of the existence of such rays. While following out the measurements of the angular diameters of the polarized rings in those experiments, it was found easy to arrive at a maximum diameter of each ring, corresponding to an extreme red illumination, but by no means so for the other end of the spectrum. Long after any sensible violet illumination continued to fall on the reflector of the apparatus, that spark of light, increasing, diminishing, vanishing, reappearing and vanishing again, as the crystal was turned round, on which the observation in question depends, would still remain obstinately visible, and the angular diameter of the polarized ring deduced from it would still go on decreasing till it became evident that there was no assigning any definite limit to the violet end of the spectrum, otherwise than by the use of a definite absorptive medium,—I mean a limit where the visible phenomena depending on continually decreasing breadths of undulation should be held to cease. It was equally evident in those experiments, that the colour of this outstanding ultra-violet ray was not properly that of any received prismatic tint; but this, at the time, I attributed to the great and progressively increasing faintness of the rays in question not making sufficient impression on the eye to allow of any decision as to their colour. This view of the matter, however, is incorrect. The following experiment will show, that these rays when so concentrated as to possess an unequivocal illuminating power, still show no *colour*, but that sort of imperfect white which is best distinguished by the terms grey, ash-colour, lavender-colour, or such expressions. As orange, indigo, and violet, vegetable tints, are used for those of the prismatic hues, I may be allowed to express by the epithet lavender the rays which produce the tint in question, rather for the purpose of abbreviating the uncouth appellation of *ultra-violet*, and avoiding the ambiguity attaching to the term *chemical* rays (which exist in all regions of the spectrum) than for that of laying any undue stress on the observed fact.

57. A spectrum from a highly refractive and dispersive flint-glass prism, the companion to the crown prism before mentioned, and, like it, the personal gift of FRAUNHOFER, of faultless purity and perfect workmanship, was thrown on the same crown lens as in the last experiment. This was purposely placed at once oblique to the incident light, and out of the plane of dispersion of the prism, or that plane to which its refracting edge is perpendicular. Moreover, it was so arranged that the spectrum might fall on any part of the lens, above, below, or on either side of its centre. Under these circumstances, it is easy to give excessive concentration to light of any given degree of refrangibility, the rest being thrown aside into long, coloured caustics. In fact, the image of the spectrum is thus bent and distorted into curvilinear forms, the general type of which may be assimilated to the letter C lengthened and flattened, with ends more or less unequal. And upon these curves, so opened or contracted,

the colours may be made to occupy any spaces, by receiving the spectrum higher or lower on the lens, and by inclining its axis more or less to the plane of incidence. Without calling coloured figures to aid our description, we may conceive the matter perhaps most readily by considering the spectrum as painted on a ring, or on some oval curvilinear form, having the eye more or less elevated above its plane, and capable of being made to revolve about its centre, the spectrum, including the chemical rays, occupying about two thirds of its circumference. If we conceive this ring, oval, or curve, projected on any plane, it is clear that the colours as depicted on that plane will have more or less concentration, according as the element of the arc corresponding to each is more or less inclined to the plane, and that where that inclination is perpendicular, the intensity at the point of projection will be (mathematically speaking) infinite in comparison with that of any other portion of the spectrum.

58. If we conceive the eye to be situated in the plane of our fictitious ring, its projection will be rectilinear, and we shall have a spectrum, as it were, doubled back on itself at any particular part of its length, and the density of the rays where this reduplication takes place will be vastly greater than at any other point. By placing the lens, therefore, so that this condition shall hold good, (which happens when its axis lies in the plane of refraction of the prism, and the spectrum falls on its principal section,) the photographic impression will exhibit in its highest intensity the effect of that particular chemical ray which is thus violently concentrated. Its illuminating power, if any, will thus also be brought into corresponding evidence.

59. By this arrangement, the colours described in Art. 54. were brought out in great distinctness, and some very striking appearances produced. Now when the ray whose chemical and optical qualities were thus especially forced into prominence was among those whose place in the spectrum, though far beyond the ordinarily visible violet, was yet within the limit of the chemical action, the portion of it thus concentrated became very apparent to the eye as a greyish-white insulated oval spot, which, when first noticed, was for the moment attributed to some accidental achromatic reflection of light backwards and forwards within the prism, an idea which the smallest movement of the prism or the lens sufficed to dissipate. But if such an idea could have been entertained after a moment's thought, the reception of the spectrum on a slip of prepared paper completely refuted it, by the intense chemical action exercised at that particular spot. The blackening, indeed, was there instantaneous, as if a red-hot body had been applied behind, or a smoky flame directed on the paper over all the space so visibly illuminated, and faithfully marking its form and degradation. A few moments of exposure sufficed to connect this spot (at first insulated) with the general impression of the spectrum, which by rapid degrees came into view. We come now to other and more remarkable results.

Chemical Properties of the Red end of the Spectrum.

60. August 27, 1839.—A highly concentrated spectrum having been formed on muriated paper, and kept for some time on the same spot, a coloured picture was formed, as in Art. 54. On examining this picture by dispersed daylight, I now for the first time noticed, that in all that part of the paper on which the full red of the spectrum had fallen, there was an appearance of whiteness, a sort of white prolongation of, or appendage to, the dark photographic impression, contrasting itself with the general ground of the paper, which, under the influence of dispersed light from passing clouds, sky, &c., had acquired a very sensible discoloration. This discoloration had, therefore, as would appear, been counteracted by the red rays of the spectrum, which are, therefore, by no means to be regarded as inactive, but rather, at least in this instance, as exciting an action of an opposite nature to that of the blue, violet, and lavender rays. To generalize this conclusion, and to assume a kind of positive and negative polarity in the spectrum, was the first and natural idea which presented itself on making the above experiment. Such a polarity had been suspected—asserted indeed—either on *à priori* grounds, or on the strength of vague and loose reasonings founded on the general aspect of many natural phenomena. But almost the very first step in the further progress of the inquiry sufficed to prove the existence of something beyond a mere opposition of qualities.

61. When paper already somewhat discoloured, by a short exposure to direct sunshine, was used to receive the spectrum, this whiteness was no longer found to be produced; but instead of such an appearance, the red tint, already noted as fringing the least refracted end of the photographic spectrum, was found to be not only much more lively, but to extend further; and instead of terminating at or near the limit where the red and yellow blend into orange, as in the Table in article 54, to encroach deeply on the space occupied by the red rays, and even, in some instances, entirely to cover that space. When, instead of exposing the paper in the first instance to direct sunshine, it was rendered considerably dark by exposing it in the violet rays of a prismatic spectrum, or in a sunbeam which had undergone the absorptive action of a solution of ammonio-sulphate of copper, the phenomenon in question was developed in great perfection; the red rays of the condensed spectrum producing on such paper, not whiteness, but a full and fiery red, which occupied the whole space on which any visible red rays had fallen.

62. In further illustration of this peculiar action, I therefore made the following experiment. On a piece of paper strongly darkened by exposure to the sun under a green glass which was ascertained to absorb every trace of the extreme red, I fastened a standard combination of glasses which transmitted *only* that red, being the identical combination described in my paper* above cited, and the same which I have always used in my experiments to insulate that ray in its utmost purity. The

* Philosophical Transactions, 1820.

paper so covered was exposed for a day to desultory and feeble gleams of sunshine, and when withdrawn and compared with a portion of the same piece of paper preserved in the dark, to have become materially less dark than before, and to have acquired a high red tint instead of the greenish blackness it had before. Papers darkened by exposure under cupro-sulphate of ammonia and by free exposure, were reddened in exactly the same way.

63. It was natural, perhaps, in this stage of the inquiry to regard, as I did, this change of tint, accompanied as it was with a diminution of total intensity, as a first step in the process of ultimate restoration to perfect whiteness, and that I should, in consequence, in the way of practical application, have forthwith proceeded to attempt the production of a *positive* photographic copy of an engraving by placing it on a frame, as usual, over a paper blackened by exposure to sunshine, covering the whole with a dark red-brown glass previously ascertained to absorb every ray beyond the orange. In this way a copy *was* obtained in effect, so far of a positive nature that the shades of the original engraving were expressed in black. But the lights, instead of *white*, were found to be eaten out in red, the colour of venous blood. Beyond this I could not succeed in pushing it, nor could I obtain any other result on exposing blackened paper under the standard red glass, however long continued.

Combined action of rays of different degrees of refrangibility.

64. It is evident from this experiment, that the conservative whitening, or oxidating action of the red rays depends on some other principle than a mere contrariety of action to that of any one species of ray in particular. It is proved, 1st, that a very powerful red ray is capable of neutralizing, *in the moment of its action*, the photographic effect of a feeble white one, in which, besides the red, are contained in due proportions all the other rays. But on the other hand, it is equally shown, that a long-continued *subsequent* action of the red rays is incapable of destroying entirely the effect of other rays once fully produced, though it superinduces on that effect the very remarkable modification of assimilating the blackness arising from their action to its own proper colour. A question of high interest therefore arose, as to what would be the effect of the combined action of a red with any other single ray in the spectrum, *if acting at the same instant*; or more generally, whether any, and what differences subsist between the joint and the successive actions of any two given rays of different and definite refrangibilities, and whether the joint action be capable, or not, of producing effects which neither of them acting alone would be competent to produce.

65. As regards the *successive* action of differently coloured rays, I have not been able to perceive, hitherto, any influence which the prior action of the less refrangible rays of the spectrum exercises in modifying the subsequent effects produced by the more refrangible. That portion of a slip of paper, for example, which has been preserved in a state of whiteness under the action of dispersed light by the long-continued action of red light, is darkened quite as rapidly, and assumes the same shade

of blackness under the subsequent influence of a blue, violet, or lavender ray, as it would have done had no previous exposure to the red rays taken place. As far as my experiments go, also, it appears that every part of the spectrum impressed by the more refrangible rays, is equally reddened, or nearly so, by the subsequent action of the less refrangible.

66. On the other hand, as regards the question, whether or not the simultaneous action of two rays of different refrangibilities be capable of producing photographic effects which neither acting separately is competent to produce, the following experiment will afford a satisfactory affirmative answer. A very fine and concentrated spectrum was formed, by receiving on an achromatic lens (by CAUCHE of Paris) of three inches aperture and twenty-six inches focal length, a sunbeam previously separated by the FRAUNHOFER flint prism above mentioned (Art. 57.). The screen on which this spectrum was received having been carefully adjusted to the correct focus, a thin flint prism of small refracting angle was interposed between the lens and its focus, so as to intercept all the less refrangible rays from the green to the extreme red, and to throw them upwards by a second refraction, thereby superposing the image of the less refracted portion of the spectrum on that of the more refracted formed by a single refraction. And by varying the place of the second prism in respect of its distance from the screen, this superposition might be made to take place at any given point of the more refracted spectrum. Things being thus arranged, a slip of muriated paper was fixed on the screen so as to receive the simultaneous action of the rays in question. The results were very striking and beautiful. The *blackening* power of the more refrangible rays seemed to be suspended over all that portion on which the less refrangible fell, and the shades of green and sombre blue which the latter would have impressed on a *white* paper, were produced on that portion which, but for their action, would have been merely blackened. But in place of the dull brick-red fringe* which would have bounded this part of the spectrum on a white ground, and in place of the white prolongation (Art. 60.) which would in that case have marked the region of the mean and extreme red, there was produced a full, rich and fiery red, occupying the whole of that region, and passing into a sombre crimson or purple, where the action of the extreme red rays ceased to counterbalance or modify that of the more refrangible ones, in concert with which they acted. The general effect was not unlike that of the succession of tints in the second series of the Newtonian rings, or rather, of the transition from the third into the second, only with a less vivid development of every colour but the red.

67. To those who may be disposed to repeat this and the following experiments, I would here observe that a polar axis driven by clockwork, to follow the diurnal movement of the sun and fix the spectrum, is indispensable. But, as the last niceties of astronomical observation have as yet no place in this research, the interrupted motion of a pendulum clock, which is fatal in such observations, is not here

* See Table in Art. 54.

felt as an inconvenience; so that by a very simple contrivance, founded on the principle of counterbalancing every part of the apparatus, and employing the clock only to regulate and controul the action of a driving weight, and *not to do the work* of putting the apparatus in motion, I was enabled with very little trouble to adapt such a movement to an axis of good workmanship which had formerly served as the support of a BIRD's quadrant. This being fixed in the proper position, carried round, diurnally, a frame on which were attached, with every necessary adjustment, the FRAUNHOFER prism, the achromatic lens and the focal screen above mentioned, as well as any other occasional and needful apparatus for varying the experiments, especially for interposing coloured glasses, and plate-glass rectangular boxes, destined for the reception of coloured and other liquids, whose absorptive action on the chemical rays it should be desired to try.

68. In my first experiments with an apparatus thus disposed, I employed a large prism of plate glass filled with water, for the sake of operating on a large beam of light. But however large the refracting angle, the dispersion of water proved too low, the spectrum being too short, in proportion to the sun's angular diameter, to give distinct and sharply defined results. It was therefore disused, and the FRAUNHOFER flint prism substituted: and here I may take occasion to mention, that whether water, crown, or flint glass was used, I was not sensible of any *peculiarity* of action (apart from difference of dispersive power) which I could fairly attribute to the qualities of those media. I confess I had looked for a contrary result, and had speculated, with somewhat excited expectation, on the discovery of bands, or interruptions, or points of maximum and minimum action in the spectrum, traceable to unequal absorption of the chemical rays by those media, though colourless. None such however appeared. But on this point I would hardly be understood to speak, as yet, decisively in the negative.

69. One of the first uses to which this apparatus was applied was an endeavour to ascertain the existence or nonexistence of fixed lines in the chemical spectrum analogous to those in the luminous, and whether corresponding, or not, in place. To this end it was necessary to diminish the sun's angular apparent diameter, which was done by affixing a small achromatic telescope with a low magnifying power, in a reversed position (eye-piece towards the sun), to receive and refract the rays before their incidence on the prism. By this means, spectra were obtained whose lengths were in a highly increased proportion to their breadths. In one experiment this proportion (as ascertained by measurement of the impression left) was so high as 67 : 1. But in this, as in other experiments where a less degree of dilatation was obtained, the interruptions, if any, to the continuity of chemical action from end to end, were so equivocal that I cannot venture to assert their existence positively, though I am led to believe it from the fact of some slight inequalities in the violet region having been repeated, in the same place of the spectrum, on shifting the paper to eliminate the possible influence of streaks left by the brush in its preparation. The only cer-

tain conclusion then that can be drawn from these trials is, the nonexistence of any *large* inactive spaces in the spectrum.

70. With the apparatus in its ordinary state, the following are the dimensions of the several principal elements of the luminous spectrum, which it will be necessary to bear in mind as data in the experiments to be detailed. They are given in parts of a scale each equal to $\frac{1}{30}$th of an inch, and are reckoned from a point, selected as a fiducial centre, at that particular definite yellow which the cobalt glass above noticed insulates in great abundance and with considerable sharpness of termination*. It was not mere caprice which determined me to depart in this particular instance from my hitherto invariable standard, the extreme red ray. The solar image in that ray is far better defined than in the yellow in question. But from many phenomena observed in the action of coloured glasses I was led to suspect, and the suspicion was borne out by the results, that this ray may be considered as marking a sort of chemical centre, a point of equilibrium, or rather of change of action, in the spectrum. In fact, in a large proportion of the preparations submitted to the action of the spectrum, that action, as far as it is marked on the paper by traces of darkness, terminates precisely, or very nearly indeed, at this point, allowing for the sun's diameter.

Dimensions, &c.	Parts each $\frac{1}{30}$ inch.
Focal length of the achromatic lens used	774
Breadth of the fixed spectrum, or diameter of the sun's image . . .	7·20
Distance *from* the fiducial point or centre of the sun's image formed by the yellow ray, 1st, *to* the centre of the image formed by the extreme red†	− 13·30
2nd, *to* that of the image formed by the mean red	− 6·66
3rd, *to* that of the image formed by the last violet transmitted by the same glass, a tolerably well-defined ray; the centre of the terminating semicircle of the spectrum judged of as well as practicable .	+ 40·62
Total length of the luminous spectrum from centre to centre of the terminating solar images	53·92

71. It would be mere waste of time to recount the almost numberless experiments on particular preparations of paper made with this apparatus, especially as they lead to no general laws. At the same time, a number of interesting facts have been encountered in particular cases; and we are led to form a very high idea of the vastness of this new field of inquiry, and the extensive bearings and connexions of any theory which shall give a rational account of these complex phenomena, from the way in which these facts, so various and so remarkable each in itself, stand insulated from one another. I shall now therefore proceed to state the phenomena observed on pre-

* See Transactions of the Royal Society of Edinburgh, 1822.

† The sign − indicates that the distance is measured towards the least refracted end of the spectrum, the sign + towards the most refracted.

senting some particular preparations to the action of the spectrum. And to begin with the simplest case, that of the nitrate of silver alone.

72. *Nitrate of Silver.* (Paper No. 570.*).—Smooth wove demy paper washed with a solution, specific gravity 1·132. The general colour of the spectrum is a rather pale brown inclining to pink, and the tint is nearly uniform, except towards the most intense part (which falls about the middle of the blue rays), where it somewhat inclines to a dark grey or lead colour, while, on the other hand, at the violet extremity of the spectrum it more inclines to pink. The total length of the spectrum impressed on white paper, as well as the insensible gradation of its most refracted end will admit of measure, is about eighty-five parts. Its least refracted termination (at which it shows no sign of red, green, or blue tints) is at — 3·2, which allowing 3·6 for the sun's semidiameter, may be considered as placing the limit of action almost exactly at the fiducial point. The maximum of intensity occurs at + 23 parts, or thereabouts; and there is a considerable indication of a second maximum at about + 43 parts, after which it degrades very rapidly, as we advance into that region of the spectrum which we have designated as the lavender rays. The feebleness of action of these rays, as compared with that of the blue and violet, is indeed the chief characteristic of this spectrum.

73. When the spectrum is made to act on paper similarly prepared, but previously discoloured by exposure to sunshine under cupro-sulphate of ammonia, the phenomena are materially different. The photographic spectrum is lengthened out on the red or negative side by a faint but very visible red portion, which extends to — 13·7, or fully up to the end of the red rays as seen by the naked eye. The tint of the general spectrum, too, instead of brown is dark grey, passing, however, at its most refracted (or positive) end into a ruddy brown. The maxima occur nearly at the same points as above stated, but that at the end of the violet is more unequivocal, and the degradation beyond it more sudden.

74. *Muriate of Soda*†. (Papers Nos. 545, 559, 568.)—The spectrum is very long, intense, and far more variously coloured than any other which has hitherto occurred in my experiments. If the paper be purely white and the day cloudless, the visible impression commences with a pretty high red at — 7·6, which at about half that distance (— 3·8) below the fiducial point begins to pass into green, through a kind of livid mixed tint. The best green, which is, however, of a sombre and dull character, is developed at or a little above the fiducial point, covering a breadth of about four parts. Thence, with a barely perceptible tinge of dark blue, it passes rapidly into intense blackness, which at + 80 begins to die away into a purplish brown, and

* These numbers refer to memoranda kept of the preparation of the various papers used.

† When one ingredient only is thus mentioned, it is understood that that ingredient has been applied as an intermediate wash between two washes of nitrate of silver; thus the preparation of the paper No. 559, on reference to the memoranda kept, appears to have been, 1st wash, nitrate of silver 1·132; 2nd ditto, muriate of soda, 1 salt + 19 water; 3rd ditto, nitrate of silver 1·096. If the word *lead* be added, it is to be understood that the first wash has been acetate of lead.

terminates the spectrum at + 90·23, making the total length of the darkened or discoloured impression 97·83 parts.

75. If there be dispersed light, the spectrum is lengthened out by a pinkish white addition extending below the fiducial point as far as − 22·43; so that the whole extent of the action on this paper is 112·66, being considerably more than double the total length of the ordinary luminous spectrum*.

76. It should be observed that, as respects the colours, the nature of the paper itself is far from indifferent. The thin paper, for example, manufactured in China, on which the books of that country are printed, is in many respects peculiar in its photographic properties, and in none more than in the comparative absence of the red and strength of the green tints produced on it, when subjected to the preparation of alternate washes of nitrate of silver and salt. The length, however, of the total spectrum is the same, but owing to the absence of the terminal red fringe, the darkened portion does not extend more than a semidiameter of the sun below the fiducial centre (thus marking a limit of action at that precise point), and the light portion is very feeble and indistinct.

Chemical Action traced much beyond the extreme Red Rays.—Exercise of a Blackening or deoxidating Power by the Red Rays themselves, under certain circumstances.

77. *Hydrobromate of Potash.* (Paper No. 571.)—Paper prepared with this salt instead of muriate of soda, gives a most extraordinary spectrum. The action commences, *the moment the rays fall upon it*, visibly over its whole length, and is uniform in intensity at every point except just at the extremities, where of course it fades gradually. But the most characteristic peculiarity of this spectrum is its extravagant length. Instead of terminating at the fiducial point, or thereabouts, *the darkened portion extends down to the very extremity of the visible red rays.* In tint it is pretty uniform (a grey-black not by any means intense) over the whole length, except that a slight fringe of redness (but no green or blue) is perceptible at the least refracted end. Beyond these evidences of deoxidation, thus traced fully up to the visible limit of the spectrum, it might be expected that all photographic action would terminate. Far otherwise; a contrary or oxidizing action now commences, marked by the maintenance of whiteness on the paper under the influence of dispersed light, and extends to a distance so considerable below the last traceable limit of the luminous spectrum, as to leave no possible room for mistake or doubt that chemical powers are exerted over a large extra-spectral region in this direction. The following statement of dimensions, a mean of three experiments, will place this important proposition in the clearest evidence. The measures are, as usual, from the fiducial point or centre of the yellow ray.

* See further on, Art. 77.

Extremity of the white portion	− 26·27
Sun's semidiameter	+ 3·60
Extremity of the chemical action in a linear spectrum or centre of the solar image in the extreme *chemical* ray	− 22·67
Centre of the solar image in the extreme *red* ray	− 13·30
Absolute extent of the chemical beyond the luminous spectrum	− 9·37
Commencement of the dull red fringe	− 15·05
Semidiameter of the sun	+ 3·60
Point in a linear spectrum to which the darkening influence would extend	− 11·45
Most refrangible extremity of the darkened portion	+ 90·50
Total length of the darkened portion	105·55
Entire length of the paper visibly affected	116·77

78. We may now observe, that this highly remarkable conclusion is also substantiated by the measurement stated in Art. 75. of the limit of whiteness on the muriated paper; for if from − 22·43, the coordinate of the termination of the sensible impression, we subduct the sun's semidiameter 3·6, we get − 18·83 for the limit of sensible chemical action on that paper in a linear spectrum* which already surpasses by − 5·5 the point (at − 13·3) at which the extreme red ray is situated in such a spectrum.

79. *Hydriodate of Potash.* (No. 577.)—The preparation of this paper is very variable in its results according to the strength of the solutions used. If strong solution of the hydriodate be used, it is nearly or quite insensible; if weak, the reverse. In the latter case the photographic spectrum it exhibits is not a little singular. It has the appearance of being inverted, the impression commencing very feebly and gradually at a point nearly coincident with the mean red ray of the luminous spectrum, where however the trace impressed is barely perceptible. Thence it gradually and regularly increases upwards till it attains its maximum of intensity at about + 50, that is to say, about five parts beyond the extreme violet. It then degrades more rapidly than it increased, till it vanishes at + 91·2, giving a total range of ninety-six parts. The tints are also remarkable. There is no imitation of the colours of the spectrum itself, but rather a kind of inversion of them. For the least refrangible end is of a dull ash grey or lead colour, and the most so, a considerably ruddy snuff-brown; the change of tint coming on rather suddenly about the end of the blue or beginning of the violet rays of the luminous spectrum.

Possible indication of Absorptive Action in the Sun's Atmosphere.

80. *Rochelle salt. Tartrate of Potash-and-soda.* (Papers Nos. 573, 574.).—Of all the salts I have examined, this presents, perhaps, the most singular peculiarities.

* By a linear spectrum I understand such a one as would be cast by a fixed star or other luminary of insensible angular diameter.

The quality of its papers however varies much with the doses of the ingredients, and, in fact, I have never succeeded in hitting again that precise proportion of the argentine and saline solutions which afforded the results I am about to state; and but that every portion of a pretty large sheet of paper agreed in giving the same, and that I have some of them now before me, I should hesitate to do so. The preparation of this particular specimen of paper, (marked 573–574 in my list of papers put on trial,) was, 1st, nitrate of silver S. G. 1·132; 2nd, saturated solution of Rochelle salt; 3rdly, nitrate of silver 1·132, which proving but little sensitive, a third wash of the nitrate was added, by which its sensibility was materially increased, its other qualities remaining unaffected. The paper was of the kind called "smooth wove demy."

81. The spectrum impressed on this paper commenced at, or a very little below, the fiducial point, of a delicate lead-colour, but faint and dilute, and when the action was arrested soon after the first impression made, such was the character of the whole photographic spectrum. But if the light was allowed to continue its action, there was observed to come on, suddenly, a new and much more intense impression of darkness, confined, in length, to the blue and violet rays, and, what is most remarkable, confined also *in breadth* to the middle of the sun's image, so far, at least, as to leave a border of the lead-coloured spectrum traceable not only round the clear and well-defined convexity of the dark interior spectrum, at the less refrangible end, but also laterally along both its edges. And this border was the more easily traced, and the less liable to be mistaken, by reason of its singular contrast of colour with the interior spectrum. That of the former, as observed above, was lead-grey: of the latter an extremely rich, deep, velvety brown. The less refrangible end of this interior brown spectrum presented a sharply terminated and regular elliptic contour, the more refrangible, a less decided one. The coordinates of its extremities may be stated at + 10·0 and + 48·5. Its length is therefore 38·5. Within this length occur two very distinct and evident maxima of intensity, viz. at + 21·7 and 36·9, the latter being by far the most conspicuous and abrupt. Another maximum also occurs beyond the limits of the dark-brown spectrum, viz. at + 56·7, in the grey or rather grey-brown colour, which the ground assumes at this end of the spectrum. The entire spectrum, including the lead-coloured portion at one end, and the grey-brown portion at the other, extends from − 3·9 to + 71·5, giving a total range of action = 75·4.

82. It may seem too hazardous to look for the cause of this very singular phenomenon in a real difference between the chemical agencies of those rays which issue from the central portion of the sun's disc and those which, emanating from its borders, have undergone the absorptive action of a much greater depth of its atmosphere; and yet I confess myself somewhat at a loss what other cause to assign for it. It must suffice however to have thrown out the hint; remarking only, that I have other, and I am disposed to think decisive evidence (which will find its place elsewhere,) of the existence of an absorptive solar atmosphere, extending beyond the luminous one.

The breadth of the border, I should observe, is small, not exceeding 0·5 or $\frac{1}{7}$th part of the sun's radius; and this, from the circumstances of the experiment, must necessarily err in excess.

Existence of a Blackening or deoxidating Power in rays BEYOND *the extreme Red.*

83. The tartrate of silver, whether *per se* or introduced into the pores of the paper by the processes above described, is by no means delicately sensitive. It remains long comparatively unaffected, and it is only when that peculiar action, above described, comes on, that the darkening process goes on with any degree of rapidity. Ultimately, however, it acquires a degree of blackness surpassing almost every other argentine compound tried. But there is a mode of accelerating this darkening and rendering the tartrated paper very sensitive, which has been already hinted at (Art. 48.), viz. by passing over it a wash of hydriodate of potash, which deserves more particular mention.

84. If while a tartrated paper, prepared with two washes of nitrate of silver, and one, intermediate between them, of Rochelle salt, is exposed to the spectrum and in slow process of darkening, it be washed over with a considerably dilute solution of the hydriodic salt, it instantly begins to blacken much faster, not only over the whole positive or most refrangible portion of the spectrum, to which the action would have been limited without this application (Art. 81.), but over all the least refrangible or negative part, and *that, not merely up to the limit of the last visible* (extreme red) *rays, but considerably beyond that limit.* The spectrum produced, however, has nothing of that singular character described in Art. 81, but is of a pretty uniform brown over its whole length. Its measured dimensions are as follows:

Negative or least refrangible limit of darkness	− 22·5
Positive or most refrangible limit of darkness	+ 67·5
Total length of the dark impression	= 90·0

There are in this, as in the un-ioduretted paper, two conspicuous maxima of the solar action, the most abrupt, which shows like an intense oval spot of about fifteen parts (or twice the sun's apparent diameter) in length, has its centre at + 37, almost exactly where the more conspicuous maximum occurs in the un-ioduretted paper, but the other, which is less definite, takes place at or near the fiducial point itself. If from the negative coordinate − 22·5 of the last perceptible blackening we subtract − 3·6, the sun's semidiameter, we find − 18·9 for the point of extreme action in a linear spectrum, which surpasses by − 5·6 parts, or by nearly the whole distance which separates the mean from the extreme red, the last ray capable of exciting the retina. It ought also to be mentioned, that when the red rays are made to act on paper thus treated, and which has already undergone the darkening action of the blue or violet rays, they do not redden it, as in ordinary cases, which seems to indicate a difference in the nature of the chemical action exerted in the above experiment.

85. The evidence obtained in this experiment of the existence of a darkening or deoxidizing power in the invisible chemical rays beyond the extreme red, or (as perhaps we ought to express it) of the reversal, by the iodic salts, of the ordinary whitening or oxidizing power exerted by those rays (Art. 60.), is confirmed by measurement of the dark spectrum impressed on the paper (No. 644.) prepared with acetate of lead and chloride of platina when washed, under the action of the light, with hydriodate of potash, as described in Art. 47, as the following statement will show.

Negative sensible termination of the spectrum	− 21·5
Subtract sun's semidiameter	− 3·6
Last efficient ray in a linear spectrum	− 17·9
Last visible red ray in ditto	− 13·3
Extent of chemical action in ditto beyond the extreme red .	− 4·6
Positive sensible termination of the spectrum	+ 70·0
Total extent of sensible chemical action	91·5

A power of precisely the same nature (i. e. of continuing the action up to and beyond the red rays,) is exercised by the hydriodate of potash also, on many other argentine compounds, as the oxalate, sulphate, chloride, &c., and probably on all.

86. The phenomenon of a triple maximum of chemical action observed in papers prepared with a tartaric salt, is also not peculiar to that class of bodies. In a paper (No. 578.) prepared with oxalate of ammonia, two very evident occur in the blue and at the extremity of the violet rays, and one, much less so, about the point where the green passes into blue. The spectrum is of a brown colour, of a dull and smoky cast at its less refracted end, but becoming livelier and more verging to a yellow at the other. *Its whole extent* lies clearly within the positive region of the solar spectrum, the sensible termination being at + 0·0, so that the place of the least refracted active ray in a linear spectrum would be + 3·6. The following are the measured coordinates.

Least refracted sensible termination	+ 0·0
Most refracted sensible termination	+ 88·0
1st. Maximum, barely traceable	+ 14
2nd. Ditto, pretty conspicuous	+ 25
3rd. Ditto, very conspicuous, and pretty abrupt	+ 41

In the spectrum exhibited on paper (No. 579.) prepared with citrate of ammonia, a triple maximum is also traceable.

Least refracted sensible termination	0·0
Most refracted sensible termination	+ 74·0
1st. Maximum	+ 24·7
2nd. Ditto	+ 39·4
3rd. Ditto	+ 56·9

The colours of the impression are smoke-grey or lead colour over the first twenty-four or twenty-five parts, and a purplish grey passing into a shade of dull pink over the more refracted portion.

87. Among the most remarkable spectra are some of those impressed on papers prepared with precipitates from liquids abounding in animal matter (such as are obtained by precipitating lead or other bodies from such liquids) applied as described in Art. 28. The paper described in the latter part of that article, when subjected to the solar spectrum, exhibited an impression whose coordinates and tints were as follows:

First sensible commencement of action at the least refracted end—*White*	− 23·0
White.	
Termination of white, commencement of faint brick red	− 5·0
Faint brick red.	
Termination of red, passing into a smoky brown	+ 1·0
Smoky dull brown.	
Commencement of a fine rich purple brown	+ 6·0
Gradually increasing in intensity to a maximum about	+ 26·0
Thence gradually declining, without change of tint, to the sensible termination of the impression at	+ 91·3
Consequently the total extent of chemical action on this paper, including the whitening or conservative action, which in this instance is marked with uncommon distinctness	= 114·3
Total length of the white portion	= 18·0

88. A precipitate consisting chiefly of phosphate of lime, but containing animal matter in combination, applied in mixture with a pretty strong solution of common salt, gave a spectrum not a little remarkable, being throughout of a uniform and very delicate lilac tint, with the slight exception of having the middle a little more verging to pink than the extremities. Its total length was ninety parts, commencing precisely at the fiducial point, and its maximum of intensity rather beyond the middle, towards the more refrangible end, viz. at + 60. When the same precipitate was applied intermediately between two washes of nitrate of silver, omitting the muriate of soda, a much more intense spectrum was produced, of a nearly uniform smoky brown or very dark grey, but peculiarly rich and velvety, barely attaining the fiducial point, and from thence, for a considerable distance, continuing extremely faint, and increasing by very gradual progress to a maximum about + 45, and decaying as gradually, but assuming at the more refrangible extremity a somewhat more ruddy hue, while at the less its tint inclined rather to a blueish or lead colour.

Effect of the Spectrum on certain Vegetable Colours.

89. The evidence we have obtained by the foregoing experiments of the existence of chemical actions of very different, and to a certain extent opposite characters at

the opposite extremities (or rather, as we ought to express it, in the opposite regions) of the spectrum, will naturally give rise to many interesting speculations and conclusions, of which those I am about to state will probably not be regarded as among the least so. We all know that colours of vegetable origin are usually considered to be destroyed and whitened by the continued action of light. The process, however, is too slow to be made the subject of any satisfactory series of experiments; and, in consequence, this subject, so interesting to the painter, the dyer, and the general artist, has been allowed to remain uninvestigated. As soon, however, as these evidences of a counterbalance of mutually opposing actions, in the elements of which the solar light consists, offered themselves to view, it occurred to me, as a reasonable subject of inquiry, whether this slow destruction of vegetable tints might not be due to the feeble amount of residual action outstanding after imperfect mutual compensation, in the ordinary way in which such colours are presented to light, i. e. to mixed rays. It appeared therefore to merit inquiry, whether such colours, subjected to the uncompensated action of the elementary rays of the spectrum, might not undergo changes differing both in kind and in degree from those which mixed light produces on them, and might not, moreover, by such changes indicate chemical properties in the rays themselves hitherto unknown. The want of sunshine has alone prevented me from pushing these inquiries to the extent to which, it will appear from the result of the only trials I have made, they well deserve to be pursued.

90. One of the most intense and beautiful of the vegetable blues is that yielded by the blue petals of the dark velvety varieties of the common Heartsease (*Viola tricolor*). It is best extracted by alcohol. The alcoholic tincture so obtained, after a few days keeping in a stoppered phial, loses its fine blue colour, and changes to a pallid brownish red, like that of port wine discoloured by age. When spread on paper it hardly tinges it at first, and might be supposed to have lost all colouring virtue, but that a few drops of very dilute sulphuric acid sprinkled over it, indicate, by the beautiful and intense rose colour developed where they fall, the continued existence of the colouring principle. As the paper so moistened with the tincture dries, however, the original blue colour begins to appear, and when quite dry is full and rich. The tincture by long keeping loses this quality, which does not seem capable of being restored. But the paper preserves its colour well, and is even rather remarkable among vegetable colours for its permanence in the dark, or in common daylight.

91. A paper so tinged (No. 599.), of a very fine and full blue colour, was exposed to the solar spectrum concentrated, as usual, (October 11, 1839,) by a prism and lens; a water-prism, however, was used in this experiment, to command as large an area of sunbeam as possible. The sun was poor and desultory; nevertheless in half an hour there was an evident commencement of whitening from the fiducial yellow to the mean red. In two hours and a half, the sunshine continuing very much interrupted by clouds, the effect was marked by a considerable white patch extending from the extreme red to the end of the violet, but not traceable beyond that limit.

Its commencement and termination were, however, very feeble, graduating off insensibly; but at the maximum, which occurred a little below the fiducial point, (corresponding nearly with the orange rays of the luminous spectrum,) the blue colour was completely discharged. Beyond the violet there was no indication of increase of colour, or of any other action. I do not find that this paper is discoloured by mere radiant heat unaccompanied with light.

92. Paper washed with an alcoholic solution of guaiacum was exposed to the spectrum formed by the FRAUNHOFER flint prism, and concentrated as usual. The paper before exposure was of a very pale yellowish colour. The action was slow, (though much quicker than in the case of the tincture of heartsease,) and extended from + 4·7, or thereabouts, to + 72·9, attaining its maximum at + 58·5, or beyond the violet, far in upon the lavender rays. The impressed spectrum throughout its whole length (68·2 parts) was of a fine celestial blue colour, though of little intensity.

93. A slip of the same paper was exposed for some time to sunshine, defended from the action of all but the blue and violet rays by cupro-sulphate of ammonia, acquiring thereby a uniform pale blue tint, verging to greenish. It was then exposed to the spectrum as in the last article. The effect was highly remarkable: the impression produced consisted of two long very faint streaks, the one, corresponding to the more refrangible part of the spectrum, from about + 42 to + 68, was of a blue colour, darker than the general ground, and having its maximum at nearly the same point as in the last experiment, viz. at + 58. The other, corresponding to the comparatively less refrangible portion of the total spectrum, commenced above at about + 27, as nearly as the extreme faintness would enable the eye to seize its beginning, and extended downwards to − 16. In this portion the blue colour of the ground of the paper was discharged more or less completely, and most so (where the original pale yellow colour of the paper was quite restored,) at − 3, that is to say upon the orange ray, and *by no means at that point of the spectrum where the caloric effect is greatest**. The effect therefore cannot be due to mere radiant heat. The neutral part from + 27 to + 42, embraces the whole of the violet and nearly all the indigo rays of the luminous spectrum.

V. *Of the Whitening Power of the several Rays of the Spectrum under the influence of the Hydriodic Salts on Papers variously prepared and previously darkened by the action of Solar Light.*

94. The singular effect of a moderately strong application of the hydriodate of potash to darkened photographic papers, in rendering them susceptible of being whitened by further exposure to light, has been already alluded to. But the prismatic analysis of this effect, as exhibited on various preparations of silver, offers a series of new relations so very curious, as may well require the bestowal on them of

* See the Notes at the end of this paper.

a few paragraphs descriptive of such very imperfect experiments as I have hitherto been enabled to make on this subject.

95. A paper (No. 646.) prepared with acetate of lead, hydrobromate of potash and nitrate of silver, when exposed, without any further preparation, to the spectrum, exhibited an instant action over the whole spectrum and down to the extreme red, beyond which appeared (the paper having been somewhat discoloured by keeping) a white circular spot to the extent of a full diameter of the sun, which though not strongly marked was unequivocal. A specimen of the same paper previously darkened to a considerable degree by exposure to sunshine, was then subjected to the action of the spectrum, and while so subjected was washed with a dilute solution of hydriodate of potash. It speedily began to *whiten* at the more refrangible end of the spectrum, the whitening commencing in the violet rays; but so far from their action being continued downwards into the less refrangible region, the paper in that region *continued to blacken* perceptibly, *and the blackening extended even below the extreme red**. A second wash of the iodic solution being now added till the paper was drenched with it, the negative or darkening action was found to be arrested in the part of the paper already acted on, while on presenting a fresh portion of the surface so drenched to the spectrum, no such action took place.

96. Similar experiments were made with various other preparations of paper, both with and without the use of lead; such as with borax, muriates of baryta, strontia and lime, sulphate and phosphate of soda, &c. It will only be necessary to detail particulars in a few cases offering peculiarities. The general mode of action seemed to be as follows. 1st. When the darkening by previous exposure to sun has not gone too far, a weak wash of the liquid hydriodate brings the paper into a sort of intermediate state, in which it continues to be further blackened, or, according to our nomenclature, has a negative character, under the action of the less refrangible rays; and that, quite down to the red end of the spectrum, and even below it in cases where, without such addition, the darkening would have terminated at the yellow ray. On the other hand, under the more refrangible rays it merely ceases to be darkened, losing its negative without acquiring a positive character. When the hydriodic application is somewhat more copious, the paper becomes under these rays distinctly positive, whitening slowly and gradually under their action, while between the darkened and whitened portions a neutral interval occurs. If a further dose of the hydriodate be applied, the neutral line descends in the spectrum, the darkening in the less refrangible portion is enfeebled, and the whitening in the more refrangible reinforced, but by no means equally. On the contrary, it not unfrequently happens that a tolerably definite portion of the spectrum, viz. just where the blue and violet join, is marked by a much more intense whitening action than that beyond it, so as to terminate the whitened portion by a conspicuous white spot. If still more of the hydriodic solution be added, or if it be applied stronger, all blackening ceases in every part of the spec-

* See Art. 85.

trum, and a white spectrum is produced, extending in some cases (but always feebly) below the fiducial point, having its maximum of intensity at the junction of the blue and violet, and fading away gradually over the more refrangible region. If the dose be very strong, the whitening goes on rapidly even without the aid of light.

97. A paper prepared with acetate of lead and then chloride of platina (neutralized by lime) was washed over, not with the pure hydriodate of potash, but with a mixed solution of this salt and tartrate of soda and potash. The action of the hydriodate was enfeebled to a greater degree than by the mere effect of dilution. It required to be excited by a second application of the liquid, and even then the darkened space, in lieu of extending to the negative extremity of the spectrum, broke off at the fiducial point. On applying, however, a third dose, the action was again excited and carried instantly down to and far beyond the extreme red. It has been already noticed (Art. 47.) that paper so prepared is insensible *per se*, and acquires a negative character under the influence of the hydriodic salts, the *gradual coming on of which character* for rays of less and less refrangibility as the dose of the saline application increases, it is the object of this experiment to trace.

98. In some instances, where, under the influence of the hydriodate, the paper has been rendered positive (i. e. whitened by light) for the violet and ultra-violet rays, and negative for the rest of the spectrum down to the red, another change of character from negative to positive has been observed to take place beyond the red, indicated by a slight but unequivocal whiteness produced about the region of the extreme red. This singular alternation of character, it may be as well to mention, occurred in two papers (Nos. 649, 656.), the one prepared with phosphate of soda, the other with muriate of strontia, both with a mordant base of lead; but it is probably not so much dependent on the peculiar preparation of the paper as on some accidental adjustment of the dose of the iodic salt in the experiments referred to.

99. In one experiment only was any other colour than mere black or dark brown, and white (or rather pale greyish yellow), observed to be produced under the influence of the hydriodic application. The paper in this case (No. 672.) had been prepared with muriate of lime and nitrate of silver without a mordant wash, and, when darkened by previous exposure and then subjected to the joint action of the spectrum and the iodic solution, was found to be negative in its character for rays more refrangible than the yellow, while in the less refrangible region it was strongly reddened. It should be observed, however, that in paper so prepared, and without the hydriodic application, the simple action of the spectrum developes an unusually strong red at the point appropriate to that colour.

VI. *Of the Analysis of the Chemical Rays of the Spectrum by Absorbent Media.*

100. As the effectual study of mixed colours, as nature presents them to us, would be impracticable by the mere use of absorbent media, unaided by prismatic analysis, so that of the photographic relations either of argentine or any other class of re-agents

would be equally unavailing, were such media alone resorted to for the purpose of effecting a separation of the luminous elements prior to their action. A combination of their analysis with that effected by the prism will lead, however, to results of no small interest. The facts I am about to recite, so far from exhausting or even systematically arranging and attacking the subject, are hardly more than sufficient to show what a singularly wide field of inquiry is here laid open to us.

101. To study this subject in its most simple form, it would be necessary to operate on some preparation which shall be equally and indifferently sensitive to every ray of the spectrum. Such a preparation, with exception of the rays beyond the extreme red, exists in the bromuretted paper of Art. 77. But when the paper used to receive the spectrum, after undergoing absorptive analysis, has its own peculiar law of sensitiveness, it is evident that the resulting impression left on such paper will be a mixed effect depending on two distinct functions, the one expressing the degree of transmissibility or *diacratic* index of the medium for that ray, the other that of sensibility in the paper to the action of such ray.

102. I have already stated that I saw no reason from experiments made with prisms of water, crown- and flint-glass, to suspect any considerable difference in those media as to their respective scales of diacratescence*; but it would be hasty on the strength of those experiments to affirm that none exists, and quite unwarranted to extend the conclusion to other colourless media. On such it was my design to have instituted a series of experiments expressly directed to this object; but the want of sun rendered it impracticable, since it is useless, or only tends to confuse and mislead, to pursue such inquiries without the use of the spectrum; and the various and striking phenomena exhibited by *coloured* media naturally gave them a precedence in point of interest. Some of the more remarkable of those which have fallen under my observation I shall now proceed to describe.

103. Red, brown, and yellow media are well known to exert their greatest absorbent energy on the more refrangible rays; and the progress from the palest yellow to the deepest red is marked by a corresponding disappearance in the spectrum, as transmitted by or viewed through such media, of these rays progressively, commencing with the violet and proceeding downward through the spectrum till only the extreme red is left. The various shades of brown seem to depend chiefly on the proportions in which the green rays are attacked in the progress of this general destruction. Nothing, however, which the eye can seize in the character of such media, in the ordinary mode of examination, indicates any tendency towards an increase of transmissibility in the ultimate violet, or anything to authorize a suspicion that rays beyond the violet would not be cut off by such media, even more energetically than the visible violet rays themselves. It is true that by those red media, whose tint verges to a rose colour or pink, both blue and indigo rays are transmitted pretty copiously; but the

* Perhaps *diacrasy* would be preferable to a term confusing, as diacratescence does, a Greek and Latin origin.

addition of a pale yellow glass to such a medium eliminates these, and converts the combination into a pure red. But the photographic character of brown and yellow media is far from conforming itself *universally* to this indication. Of this the common yellow and brown glasses which are met with in the shops afford a striking example. The spectra impressed by transmission through such glasses consist of two distinct portions, separated by a larger or shorter interval, and having themselves a less or greater extent and intensity in proportion to the depth of tint of the glass. If that tint be only a pale yellow or straw colour, both portions are finely developed. If in that case the exposure be long continued, the continuity of the spectrum is maintained by a feeble train of darkness in their interval. Abstraction made of this, the most refrangible portion may be stated to commence precisely at the end of the violet, or at + 40·6, whence it increases gradually to a maximum at + 60, and thence dies gradually away, till it ceases to be traceable at + 85, giving a range of forty-four parts in the ultra-violet rays for its extent. The interval between the portions measured in the same experiment from which the foregoing numbers are taken, and a similar abstraction made of the faint connecting train of darkness, was twenty-three parts, occupying the whole space, which in a complete spectrum would have been filled with violet and indigo light. The least refracted portion, commencing at + 18, rapidly attained the full intensity it would have had if freely exposed without the yellow glass, and from thence to − 11, where it terminated, offered the same successive tints (dark blue, green, and red, the paper having been prepared with muriate of soda) which it would have done in those circumstances. As to the tint of the ultra-violet portion, it was a fine violet-purple without any variation.

104. When the colour of the glass used was a pretty strong brown, such as to cut off all the violet, indigo, blue, and the greater part of the green, the ultra-violet portion of the photographic spectrum, though much enfeebled and contracted, was still distinctly traceable from + 58 to + 83, the maximum (at + 70) being considerably more remote than in the former case, and this might be owing to an actual difference in the colouring matter of the glasses. On the other hand, the less refrangible portion had shrunk to a small and well-defined oval spot, extending from + 3·5 to − 9·5, or over thirteen parts, or rather less than two diameters of the sun, having its upper part coloured lead-grey, the lower red.

105. One of the finest and most brilliant yellow liquids with which I am acquainted for purposes of absorptive analysis, is the solution of that substance to which DALTON has given the name of quadro-sulphuret of lime, and which is easily prepared by boiling lime and sulphur together in plenty of water. Its transparency is so great and its tint so luminous a yellow, that it scarcely seems to impair the brightness of white objects seen through it in thicknesses of an inch or two. But its action on the more refrangible end of the spectrum is very energetic, and at a thickness = 1·1 inch was found to be such as to limit the visible spectrum to an extent of 33·2, including the two terminal semidiameters of the sun. Only a faint trace of blue was visible at the

more refrangible end. And to these indications the photographic spectrum was found to correspond, being reduced to an oval patch not exceeding nineteen parts in extent, between the limits + 13·5 and − 5·5, and that, it should be observed, of a uniform tint, the red fringe at the least refracted end (which was pretty conspicuous on the paper used when subjected to the unimpeded spectrum) being deficient, from which it may be surmised that this liquid acts more powerfully on the chemical rays at the red end of the spectrum than on the luminous. The contrast between the complete and absorbed spectra in this experiment was indeed most striking, considering the small apparent loss of illuminative power. The unabsorbed spectrum extended from − 8·0 to + 87, or over ninety-five parts, throughout fully sixty-five of which its intensity was uniform, and its hue deep black. A like degree of blackness extended only over thirteen parts of the absorbed spectrum, so that while the illuminating power of an incident sunbeam was so little impaired by the action of the liquid as already stated, its total photographic effect must have been diminished by the loss of at least four fifths of its amount. It should also be mentioned that in this experiment there was not the least trace of the action being resumed in the region beyond the violet rays.

106. The singular properties of nitrous gas pointed out by Sir David Brewster as exhibited in its absorbent action on the spectrum, which it breaks up through its whole extent into alternating bright and dark spaces, led me to expect some equally singular affection of the photographic spectrum after undergoing its absorption. But this expectation was not fulfilled. The photographic impression was reduced by the action of a glass globe filled with this gas, to a small extent (twenty-five parts) by the destruction of all action beyond the blue rays; but in what remained I could discern no trace of interruptions of continuity. The experiment, I should observe, however, was difficult, having no means of drying the gas at hand, so that to prevent the deposition of moisture the globe was obliged to be frequently heated. It would be desirable therefore that it should be repeated, and that other absorbent gases should also be tried.

107. Another and no less striking example of the independence of the laws of absorptive action of media as exerted on the chemical and luminous rays, is afforded by the cupro-sulphate of ammonia. That beautiful liquid, as I have shown in my paper above referred to*, acts with the greatest energy on the red end of the spectrum, which it completely obliterates in a very small thickness, the action diminishing progressively till it seems reduced almost to nothing at the more refrangible extremity. Its scale of diacratescence, however, is quite different from what this indication would lead us to expect. The absorptive action on the chemical, as on the luminous rays indeed, at the less refrangible end, is intense, and goes on diminishing progressively to about the middle of the indigo, but here it begins again to be reinforced, and attains an energy in the region of the extreme violet, and over the whole extent of the

* Transactions of the Royal Society of Edinburgh, 1822.

yet more refracted rays, sufficient to destroy all photographic action over that part of the spectrum, and to confine its effective range between the limit of the green and blue rays on one hand, and the extreme violet on the other.

108. A green glass limits the photographic spectrum to a short oval patch extending from the fiducial point, or a very little below it, to + 18 or 20, in which no coloured fringe can be traced. The glass used was of a pure grass green hue of considerable intensity, neither verging to the yellow on the one hand nor to a blue on the other. When sulphate of nickel was used, the impression was of somewhat greater extent in both directions, viz. from about − 3 to + 28; but in both cases the action of the indigo and violet rays, and of all beyond them, was totally cut off.

109. Among dichroïte media (or those which in some certain thickness insulate two portions of the luminous spectrum, or which are much more eminently transparent for two rays than for all the rest,) there is none more remarkable than the muriate of chromium*, which reduces the spectrum to two narrow and pretty well defined spaces, coloured, the one red and the other green, the red being that at the extremity of the spectrum, and the green of great purity and richness of tint. Nor is the action of the spectrum thus analysed on photographic papers less remarkable. On such paper (prepared with common salt) it impresses, under a considerable thickness of the medium, two circular spots, the one intensely black, the other white, the places of whose centres coincide with those of the coloured images, exactly in the green, and nearly so in the red, only somewhat lower, indicating the action of invisible rays. When the liquid is more dilute, or the thickness diminished, so as to render the coloured images perceptibly oval, these spots, in like manner, extend into ovals, and moreover, a third, much fainter, makes its appearance in the region beyond the violet, where no perceptible illumination falls. As the liquid is more diluted, or its thickness more reduced, this spot gains strength, and connects itself by a faint train of darkness with the much more intense one corresponding to the green image. In like manner also may the cobalt-blue glass already so often spoken of, which is in effect a polychroïte medium, be made to insulate a definite circular white spot in the photographic impression of its spectrum, corresponding to those extreme red rays which it insulates in such perfection. To return, however, to our chromic solution It is impossible not to be struck with the much greater energy of chemical action in the green which this medium insulates, than with that insulated by the green glass already alluded to; and the following experiment presents us with a green of considerable illuminating power, which is almost or quite devoid of chemical action.

* Vide article LIGHT, Encyclopædia Metropolitana, under the head of Absorption, where the curious properties of this medium were, I believe, first pointed out. At that time I regarded them as unique, for the dichroïte action of sap-green is not nearly so definite; but I have since found the same property in two other liquids, viz. in a sulphuric solution of sublimed indigo diluted with alcohol, and in a sort of ink sold under the name of STEPHEN'S Writing Fluid: the green in this last, however, is less pure and definite; and it differs also from the other two in extinguishing the red with more energy than the green, in consequence of which its ultimate tint is green, while that of the others is red.

110. The colouring matter of archil is in many respects highly remarkable. It may be insulated by precipitating the ammoniacal liquid, commonly sold under that name, by dilute sulphuric acid, washing the insoluble matter which falls, redissolving in very dilute carbonate of soda, and again precipitating. It is very sparingly soluble, if at all, in water, but most readily so in all alkalis, which take up an enormous quantity, and afford solutions of the most intense conceivable purple colour. To this colouring principle, which, like others of the same class*, has many of the characters of a weak acid, the name *Rocellic acid* (*Lichen Rocellus*) may be not inappropriately applied. The rocellate of potash, greatly diluted, transmits a spectrum which may be considered as typical of those afforded by purple media, the yellow ray being attacked with peculiar energy, and entirely absorbed by a very small thickness or density of the medium. When a spectrum so transmitted was received on muriated photographic paper, it was curtailed both at the most and least refrangible end, and reduced in its extent to the space included between the coordinates + 8 and + 72. Allowing therefore 3·6 for the sun's semidiameter, it appears that the rays in the linear spectrum as far as + 11·6 from the fiducial points, were rendered inactive. Yet so far from the luminous rays being extinguished in this interval, so dilute was the solution used, that a great quantity of green light occupied the undarkened space in question, such as, had its properties not been altered by the medium it had traversed, could not have failed in the time the exposure lasted, to have produced a considerable blackening of the paper. That produced by the *unabsorbed* spectrum over the same region was very intense, as is always the case with muriated preparations of paper.

111. The faint spot beyond the violet produced in the spectrum which has undergone the action of the muriate of chrome, may possibly have some direct connexion with that peculiar illuminating ray to which the epithet lavender has (whether properly or not) been applied in the foregoing pages. At least I find that, on viewing the oval spot of that light (concentrated as described in the earlier part of this paper by a prism and inclined lens) through various coloured glasses, it is not absorbed by either green or yellow glasses sufficiently deep to obliterate the *whole of the violet*; and, what is extremely remarkable, such glasses, by suppressing in a most decisive manner the violet illumination in this part of the spectrum, and by defending the eye from extraneous light, reveal the existence of a faint but evident substratum (so to speak) of unabsorbed light, of a similar character, connecting the spot in question with the rest of the spectrum; unless, indeed, which is not impossible, this be merely

* Such as the colouring principle of the common Heartsease, which, as the experiment described in Art. 90. proves, has, like that of archil, a deoxidated form; that also which abounds in the black ebony wood, and which is easily extracted from it by decoction in water, and precipitation by nitric acid, &c. I may be allowed to mention that the name, and the chemical process described in the text, are taken from notes of experiments made on archil in September, October, and November 1829, while ignorant that the subject had engaged the attention of Robiquet, whose elaborate memoir on that Lichen appeared in the Annales de Chimie about that time, thereby preventing the publication of my experiments; some notice of which, however, by M. Quetelet, appeared in the Journal des Sciences de l'Acad. Royale de Bruxelles, (Seance du 22 Mai, 1830.).

the most refracted extremity of the spectrum doubled back on itself. On the other hand, this spot *is* absorbed by cupro-sulphate of ammonia, which also attacks the green, as well as by a rose-coloured glass, which lets the blue rays pass in abundance, but destroys both the green and violet.

112. In further illustration of the action of coloured media, I may mention here some very curious results which have been communicated to me by Mr. Hunt above mentioned, and which I have his permission to insert. They seem to indicate some peculiar action of the barytic salts, but the habitudes of the media employed with relation to the pure prismatic rays not being stated, it is impossible to refer them to their precise origin in the spectrum.

"A paper," says Mr. Hunt, "prepared by washing with muriate of barytes and nitrate of silver, allowed to darken whilst wet in the sunshine to a chocolate colour, was placed under a frame containing a red, a yellow, a green, and a blue glass. After a week's exposure to diffused light, it became bright red under the red glass, a dirty yellow under the yellow, a dark green under the green, and a light olive under the blue.

"The above paper, washed with a solution of a salt of iodine, is very sensitive to light, and gives a beautiful picture. A picture thus taken was placed beneath the above four glasses, and another beneath four flat bottles containing coloured fluids. In a few days, under the red glass and fluid, the picture became a dark blue, under the yellow a light blue, under the green it remained unchanged, whilst under the blue it became a rose red; and now, after three weeks, this red is slowly changing to green.

"I took a copy of an engraving under the glasses with the same paper. There was no action beneath the red glass, not much beneath the yellow, but beneath the blue it was very perfect, and, strange to say, beneath the green glass every line was faithfully copied; but the dark parts of the engraving were the brightest of the copy, as if it had been taken on one of the white photogenic papers."

VII. *Of the exalting and depressing Power exercised by certain Media, under peculiar circumstances of Exposure to Solar Light, on the Intensity of its Chemical Action.*

113. When thin post-paper, merely washed with nitrate of silver, without any previous or subsequent application, is exposed to a clear sunshine, partly covered by and strongly pressed into contact with glass, and partly projecting beyond it, so as to be freely exposed to air, the darkening produced in a given time is very unequal in the two portions. That protected by the glass, contrary to what might have been expected, is very much more affected than the part exposed; more, indeed, in some instances, than would be produced by free exposure during three or four times the given time. When fixed by hyposulphite of soda, the difference is rendered yet more striking, to an extent hardly credible without trial.

114. This singular effect was observed at the very outset of my inquiries, and was

noticed in my first communication to the Royal Society. It was attributed at first successively to a variety of causes, such as retention of aqueous vapour, reflection backwards and forwards of the incident light between the surfaces of the glass and paper, to a development of heat at the point of contact, disengagement of gas, &c. None of these causes, however, appear adequate to account for the observed effect. Mere moisture has but little influence on argentine papers. The additional light returned on the paper by continued reflection is much too small, and this explanation is opposed by the observed fact, that the effect in question is imperceptible in a gloomy day, however long the exposure be continued, and that it increases in degree as the sun is stronger. This would certainly favour the idea that the cause is to be sought in heat developed and retained by the glass; and this explanation may appear to be supported by the fact, that the effect in question is not produced when the glass, instead of being pressed into contact with the paper, is merely placed before it as a screen, with a considerable interval between them. When a piece of nitrated paper, for instance, was rolled round a cylindrical surface of moderate convexity, covered with black velvet, and the glass gently laid in contact with it, the effect of sunshine was exalted at the line of contact; but on either side of that line, as the interval increased, the influence of the glass diminished, and at less than half an inch distance no difference could be perceived between the impressions under the glass and in free air. Nevertheless, on trying to produce the same effect in gloomy days, by heat alone applied to a metal plate in contact with the paper, no increase of action was observed unless the heat was fully that of boiling water. But this is far greater than can be acquired, under the circumstances of the experiment, by the mere action of the sun. Moreover, I find that the same exalting effect is produced when a thin close-textured white paper is interposed between the nitrated paper and the glass, and *that* when the sun has far from its full power; under which circumstances only a very moderate warmth can be excited at the point of action.

115. *When first this phenomenon was noticed, the idea was suggested of two opposing influences in the solar light, the *difference of which only* becomes sensible in the immediate chemical effect, and of which the negative or deoxidizing one (using the term in a mere conventional sense) is partly stopped by the glass. In pursuance of this notion, red light, concentrated by a lens, after reflexion at the surface of a looking-glass, was thrown on paper exposed to the free sunshine, but without any perceptible effect in retarding its discoloration.

116. In further prosecution of this subject I fastened (March 24, 1839,) on a piece of nitrated paper, colourless, or nearly colourless plates, of the following substances:

* This paragraph is copied verbatim from my first communication on this subject. The paper used was nitrated, the sun feeble, and all circumstances unfavourable, (February 10, 1839). Had muriated paper been used, however, the experiment so conducted could have hardly failed to have verified (at least so far as it goes) the peculiar views of solar action which suggested it, and thus to have led to the earlier discovery of those singular properties of the less refrangible rays described in the foregoing part of this paper.

1. Saxon topaz, parallel to the axis. } These plates had a very slight purplish tinge.
2. Saxon topaz, perpendicular to the axis. }
3. Sulphate of lime.
4. Iceland spar, a natural rhomboid.
5. Plate glass, slightly tinged with blueish green.
6. Rochelle salt, parallel to the axis (not very well polished).
7. Thick quartz, perpendicular to the axis.
8. Thin quartz, perpendicular to the axis.
9. Thin quartz, oblique to the axis.
10. Thin quartz, differently oblique to the axis.

After exposure to the sun for a sufficient length of time to darken the ground of the paper considerably, it was found on taking off the plates and fixing the whole with hyposulphite of soda, that all the substances employed had considerably exalted the solar action, though not all in the same degree. The plate-glass, which, as observed, was a little coloured with blueish green, had produced decidedly the greatest effect, the discoloration beneath it being at least three or four times that of the general ground of the paper. The order of the others was as follows:

Nos. 7, 4 . . . . 6, 8, 3, 10 . . . . 9, 2, 1,

which, on the whole, was nearly that of the thicknesses of the plates, and does not seem, except in the case of the glass, to indicate any *peculiar* action in the media; and in this case the slight tinge of green, by stopping the chemical rays beyond the red*, may be supposed to have increased the action.

117. At the same time that this experiment was made another circumstance was noticed, which added to the obscurity of the subject. A specimen of paper, infinitely more sensitive than the nitrated paper I at that time used, was sent me by Mr. Talbot. This paper, treated exactly in the same manner, and exposed at the same time with a specimen of the nitrated paper, exhibited no such exalting effect. This induced me to subject, at various periods, to similar trials a great number of preparations and several varieties of paper, the results of which appeared exceedingly capricious, as in some cases it was found that exactly the reverse effect was produced, and that the superposition of one and the same glass in several instances exercised *quite as remarkable an influence in depressing, as in others it did in exalting the solar action*; while in others, again, it seemed to exercise no influence at all. The quality of the paper, too, appeared to exercise a marked influence on the result. And differences in the mode of preparation, and the doses of the ingredients, too minute to be noted, would alter materially the degree, and sometimes even the character of the effect. The following Table contains several of the results of these trials. Column 1. contains the number of the paper; column 2. the character of the effect, in which + indicates an exalting influence on the glass, 0 indifference, and − a depressing in-

* See Art. 77.

fluence; repetition of the sign indicating a greater intensity of the observed effect, whether exalting or depressing. The third column gives the characteristic ingredient of the chemical preparation used for rendering the paper sensitive, and the fourth the description of paper employed.

No. of Paper.	Character of Effect.	Characteristic Ingredients of Preparation.	Sort of Paper.
12	+ + +	Simple nitrate of silver	Thin post, of very even texture.
694	+ +	Ditto	Unsized white paper.
570	0	Ditto	Smooth demy.
583	+ + +	Borax	Smooth thick wove post.
614	0	Ditto	Smooth demy.
593	+ +	Tartrate of antimony	Thick wove post.
598	+ + +	Rochelle salt	Smooth demy,
582	+	Phosphate of soda	Thick wove post.
580	+	Hydrocyanic acid	Smooth demy.
581	+	Bicarbonate of soda	Thick wove post.
571	0	Hydrobromate of potash	Smooth demy.
	0	Unknown, but supposed hydrobromate of potash	Specimen prepared by Mr. Talbot.
545	— —	Muriate of soda	Thick wove post.
550	—	Ditto	Thin post.
547	0	Ditto	Ditto.
556	+	Ditto	Smooth hotpressed note-paper.
584	—	Ditto	Chinese paper.
603	+	Ditto	Thick post, a different sort from 545.
607	0	Ditto	Smooth demy.
623	— — —	Ditto	Blue wove post.
579	—	Citrate of ammonia	Smooth demy.
578	— —	Oxalate of ammonia	Ditto.
609	— — —	Muriate of soda over acetate of lead	Ditto.
610	— — —	Muriate of soda over nitrate of lead	Ditto.
613	— — —	Phosphate of lime precipitated from solution of nitrate of urea	Ditto.

Whether these facts have any connexion with the properties of colourless liquids discovered by M. Malaguti, I am unable to conjecture, my knowledge of his experiments being derived merely from verbal report.

VIII. *Description of an Actinograph, or self-registering Photometer for Meteorological purposes.*

118. As I do not mean this paper for a regular treatise, as on the contrary it pretends only to be a mere collection of insulated facts, observations, and processes, I may be pardoned for inserting in this place an application which very early suggested itself, and which, as far as I have tried it, proved satisfactory in its working, viz. that of a self-registering meteorological photometer or *actinograph*. The objects of such an instrument, which cannot but be one of material importance to the meteorologist, the botanist, and the general physiologist, may be considered as two-fold, viz. 1st, to obtain a permanent and, at least, self-comparable register and measure of the momentary amount of general illumination in the visible hemisphere which constitutes daylight; and 2ndly, to obtain a similar register of the intensity, duration,

and interruption of actual sunshine, or, when the sun is not visible, of the illumination of that point in the clouded sky behind which the sun is situated.

119. To accomplish the first of these objects, it would be necessary, in strictness, to expose the photographic paper destined to receive the register, to a full uninterrupted view of every part of the sky, that occupied by the sun's disc alone excepted, which would not be very easy to accomplish, without a somewhat complicated apparatus, to cut off the direct solar rays, by a moving screen of the requisite diameter. But if we consent to sacrifice the light of the zone of the heavens traversed by the sun in its diurnal motion, and such other small portions as may be intercepted by a slight frame-work, nothing is more easy. Let a weather-proof box or case be constructed, within which a clock-motion shall carry round, once in twenty-four hours, a cylindrical barrel having its axis horizontal, and its upper surface close to the under surface of the top of the box, which at this point must be thin, and pierced with a narrow oblong window bevilled off at the edges so as to admit light from every part of the sky (but what is intended to be screened) to fall on that part of the circumference of the cylinder which travels close beneath it. The cylinder then being daily covered with a strip of sensitive paper, will of course register the total illumination which the slit admits to fall upon the paper, that is to say, the light of the hemisphere *plus* the direct sunshine if the latter be not intercepted. To accomplish this nothing further is needed than to adjust a light cylindrical hoop of brass to slide smoothly but stiffly up and down along three straight, parallel steel or brass rods, of no greater diameter than is necessary to give the requisite strength ; the direction of which shall be towards the pole of the heavens, and whose places shall be such that the axis of the hoop shall pass through the middle of the exposed area of paper. The upper ends of these rods should terminate in and be connected by a strong brass ring sustained by a vertical pillar; the lower must be fixed to the pedestal or other support of the clock and its case, on which also the pillar above mentioned must be fixed. It is evident then that at any time of the year, or whatever be the sun's declination, if the hoop be adjusted and clamped so as to throw its shadow across the window at one moment of the day, it will do so throughout the whole day, and the proper place for each day in the year may be marked on the rods.

120. This contrivance, though convenient, and necessarily effectual, is not that which I ultimately adopted, which is as follows. A spring watch belonging to a 'SGRAVESANDE's heliostat (as constructed by ROBINSON) has a hollow axis for the hour-index passing completely through it, from face to back, so as to permit a steel axis, removable at pleasure, to traverse it, and issue below. It is mounted on a stand so as to admit of adjustment both in altitude and azimuth, the former by a small divided quadrant and vernier, and so placed (according to the intention of its original use) as to have the upper surface or dial-plate of the watch parallel to the equator, and of course the axis of the hour-index directed to the pole. On this axis, and at the upper surface of the watch, was fastened a disc of sensitive paper, attached to a

light circular card (to keep it flat) by slight touches of soft cement. This appendage was brought as close as possible to the dial-plate, avoiding contact, and was of course carried round uniformly once in twenty-four hours by the rotation of the axis. Over this a shade or cover was adapted, having an aperture in the form of a very narrow sector of the circle, to admit the light. If the paper be as sensitive as it ought, the smallest chink suffices, an amplitude of a degree in angular subtense at the centre being more than enough. The edges of the aperture should be so bevilled, or otherwise defended by screens, as to admit no direct ray of the sun when north of the equator, nor any other light than what emanates from that definite circumpolar region of the sky to which it may be considered desirable to limit the observation, such as, for example, a circle whose semidiameter shall equal the latitude of the place in extratropical countries; unless we prefer to register the actual illumination of the sky at the pole, in which case a tubular screen pointed to the pole must be adapted to the whole apparatus. Under these circumstances, we shall find at the end of each day the changes of illumination registered on the sensitive paper by a fan-shaped alternation of light and shade, radiating from the centre over so much of the area of the circular disc of paper as corresponds to daylight, or to such twilight as the paper is sensitive enough to be discoloured by. Of course it will be recollected in reading this description that the pole is the only point in the hemisphere whose illumination is independent of the sun's hour-angle, and which can therefore properly be taken as likely to afford an average of the clear or cloudy state of the sky.

121. For registering the *direct* effect of solar radiation it is necessary, 1st, that the paper should at every moment be presented at right angles, or nearly so, to the incident beam. The greatest inclination of a sunbeam, however, not exceeding $23\frac{1}{2}$ degrees to the equator, a paper wound on a cylinder having its axis pointed to the pole will always fulfil this condition near enough, the difference between the cosine of that angle and radius being only eight per cent.; and the error being, moreover, one susceptible of allowance by a trifling calculation, or by a table, being the same for the same day in every year. Moreover, as the sun travels round in its diurnal course, and is required to throw a limited beam in succession on every part of the paper, it is clear that the cylinder on which the paper is fastened must either remain fixed in darkness, while a cover having an aperture to admit the ray revolves at the same rate as the sun, or else the cylinder must be caused to revolve in the same direction as the sun, but with double the velocity; this last condition, however, would induce needless complication into the wheelwork of the mechanism. The simplest mechanism I have been able to devise, which meets all the conditions, is as follows.

122. To the lower end of the steel rod which penetrates the axis of the hour-index of the watch described in Art. 119, must be firmly adapted a hollow cylinder of thin and light material, as very thin sheet-brass, closed at that end which is attached to the steel rod, but open at the other, and having its axis coincident with the prolongation of the rod. In one side of this cylinder, viz. on that which corresponds to

the hour-angle 0 of the index-hand, must be cut a very narrow longitudinal slit, commencing at the closed end, and extending down somewhat less than two thirds the length of the cylinder, to admit the sunbeam. And it is evident that if this slit be so placed at any moment of the day that the sunbeam admitted through it shall strike the (imaginary) axis of the cylinder, it will do so all day; and that this will take place in the arrangement proposed, if the watch be set to show the correct hour-angle.

123. But in place of freely traversing the hollow of the cylinder, the ray is to be received, immediately on entering the slit, on a band of sensitive paper rolled round an interior *fixed* wooden cylinder, concentric with the other, and barely leaving room for the exterior revolving cylinder to escape contact in every part. This is easily accomplished by forming this interior cylinder of solid wood, bored along its axis, and causing it to travel smoothly along a cylindrical mandril of sufficient strength and solidity of support at its lower end to keep it always well in its true polar direction. For convenience of taking off the old and adapting new papers, this mandril may be furnished with a hinge at its lower end, which, however, must be very strong and of good workmanship; so that being turned back to a proper angle, the wooden cylinder it carries may be enabled to slide entirely off it at its upper end, and in so doing clear the lower rim of the hollow cylinder. Supposing the mandril in this position, the paper fixed round the upper end of the wooden cylinder, the latter replaced on the mandril and thrust down far enough to clear as above mentioned; the mandril must be then restored to its polar direction by turning on its hinge till it abuts against a fixed obstacle, and the wooden cylinder with its paper must then be slided up it till its upper end shall be very near to, but not in contact with the close upper end of the hollow revolving cylinder: and in this situation it is to be pinned or clamped fast. To prevent admission of light between the hollow exterior and wooden interior cylinders, the latter should be formed with a projecting shoulder and metal cylindrical guard-rim, which shall in its turn, when slided up as aforesaid, externally surround the lower part of the hollow cylinder, coming up, all round it, almost to the lower end of the slit which admits the sunbeam. A glance at Plate I. will explain whatever may appear obscure in the description of this mechanism. The others require no illustration. I ought to state that it is the second only of these contrivances that I have actually executed.

Reference to Plate I.

A. The steel axis carried round by the clockwork in twenty-four hours.

B. The hollow brass cylinder open at its lower end to admit the upper portion of the wooden cylinder I.

C. The slit to admit a sunbeam, covered with clear plate-glass.

D. The mandril revolving on the hinge E, and having, when in its working position, its axis coincident with that of the steel rod A and cylinder B.

E. The hinge in east and west azimuth.

F. The obstacle forming part of the bed G H of the apparatus destined to sustain the mandril D at its correct elevation.

G. A similar obstacle to keep it from tilting inconveniently far, when thrown back to take off the wooden cylinder.

H. The bed of the apparatus.

I. The wooden cylinder sliding on the mandril D, and shaped off for lightness at its lower part.

K. The band of sensitive paper rolled round it.

L. An exterior cylindrical guard to cut off light when the cylinder is slided up to its place on the mandril and clamped there, and to prevent the entry of rain below.

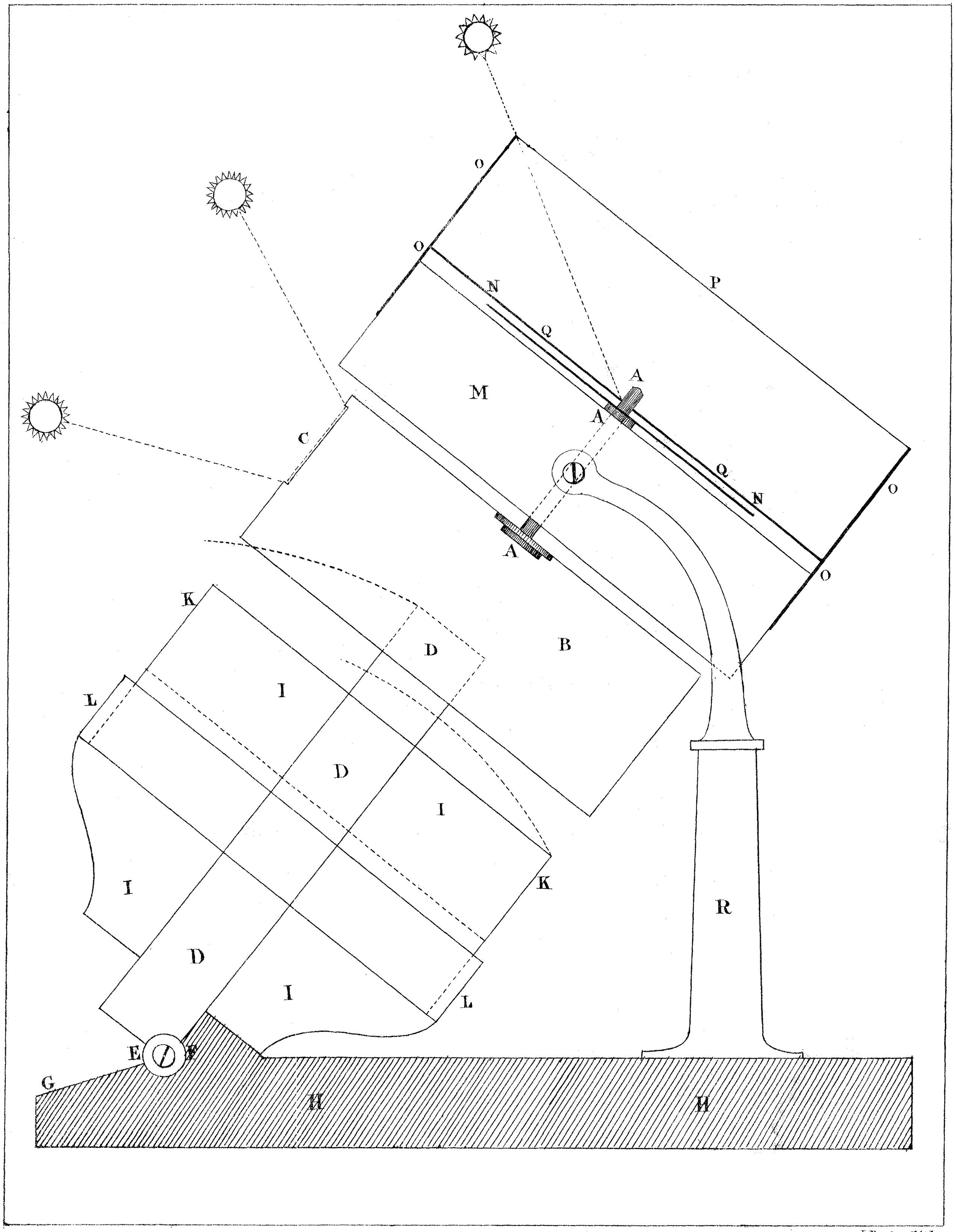
M. The weather-tight case, containing a spring clock to drive the axis A.

N. The disc covered with sensitive paper.

O. A close-fitting cover to defend the clockwork from rain, glazed with clear plate-glass at its upper surface P, well cemented. The cylindrical rim acts as a guard to keep the sun's direct rays from striking on the sensitive paper.

Q. A brass diaphragm in the cover O, in which is cut the sector-shaped slit for admission of light, having its direction from the centre of the dial-plate to the hour-line of noon.

R. The pillar supporting the upper works.



J. Basire, lith.

Note I.—*On the Distribution of the Calorific Rays in the Solar Spectrum.*

Received March 4,—Read March 5, 1840.

124. Since the communication to the Royal Society, of the foregoing pages, I have discovered a process by which the calorific rays in the solar spectrum are made to leave their impress on a surface properly prepared for the purpose, so as to form what may be called a thermograph of the spectrum, in which the intensity of the thermic ray of any given refrangibility is indicated by the degree of whiteness produced on a black or very dark ground, by the action of the ray at the point where it is received at the surface. From the nature of the process it is demonstrable, that only rays of *heat*, and not those which are usually called chemical, can be concerned in the effect produced.

125. It is easy to see what a variety of interesting applications this lays open to those engaged in studying the subject of transcalescence, whether in its relations to coloured or colourless media. As a specimen of what may be expected from the mode of observation in question, I shall proceed to describe the thermograph of a spectrum transmitted, 1st, through the prism of FRAUNHOFER's flint-glass, described in Art. 57 of the foregoing paper; and 2ndly, through the flint- and crown-lenses of the achromatic object-glass, there also mentioned; premising, however, that the observations were made in occasional and by no means powerful gleams of sun, in a day generally and densely cloudy.

126. Recurring to the dimensions and signs of the former articles, used in describing the chemical and luminous spectra, the thermograph in question consists of a white streak of the breadth of the sun's diameter, extending, where broadest and best defined, towards the positive or more refrangible end of the spectrum, to about + 25 or 30 parts, (of which the old Newtonian spectrum, taking in the extreme visible colours, occupies 54,) but fading away with great rapidity, and at the point so indicated no longer traceable, a point corresponding to about the end of the brighter blue rays. On the negative or less refrangible side of the fiducial yellow, however, it goes on increasing to a maximum at − 16, that is to say, 3·2 parts beyond the extreme red ray. (The dimensions here referred to are reduced to a linear spectrum, or to one formed by a luminary having no sensible diameter.) Beyond this maximum, the intensity of whiteness decreases *to a minimum* at − 31, where it is nearly evanescent, but immediately again recovers, so as to form a faint but unequivocal whitened solar image, *insulated from the rest of the thermic spectrum*, whose centre is situated at − 35; thus imitating, in a certain sense, the coloured spectrum of the cobalt-glass, in which a faint and otherwise indiscernible red ray is insulated from the rest of the coloured spectrum.

127. If any doubt should remain in the minds of photologists as to the correctness of my father's results, which placed the maximum of heat beyond the last visible red,

the ocular evidence of their effects thus afforded must at once set the question at rest. But the extent to which the thermic rays thus traced, overlap the luminous and even the chemical or oxidizing rays, is, I must confess, to myself quite unexpected.

128. If we take in the calorific effect at the least refrangible or negative end, and the chemical at the positive end of the spectrum, the one as traced in the above experiments, the other as in the photographic spectrum of bromuret of silver (Art. 77.), i. e. from -35 to $+86{\cdot}9$, we have a total of $121{\cdot}2$ for the extent over which dispersion scatters the sun's rays, reckoned on a scale of which the Newtonian coloured spectrum occupies $53{\cdot}8$ parts, or considerably less than one half: and that this is not yet the full extent of prismatic dispersion is highly probable, since the insulation of the terminal thermic image can hardly be considered in any other light than as a result of absorbent action in one or all the glasses through which the rays have passed.

Note II.—*On a definite limit of Photographic Action of the Blue Rays under the influence of an Iodic Salt.*

Received and read with Note I.

129. A spectrum was formed on paper (No. 606.) prepared with alternate washes of nitrate of silver and common salt; and this action was continued till the impression became very intense. *Without dismounting it, or in any way displacing the spectrum from exact coincidence with the photographic image*, it was washed under the continued action of the light, with a moderately dilute solution of hydriodate of potash. The action immediately began to be reversed at the more refrangible end, and as far as the junction of the blue and indigo rays, or rather, to speak more distinctly, as far as $+25{\cdot}0$ in the actual, or $+21{\cdot}4$ in the linear spectrum. After continuing the action a short time, the whole of the more refrangible end of the photograph, up to this limit, was eaten away, the limit being marked by a tolerably sharp and well-defined semicircular outline, while below, the effect was hardly to deteriorate the impression produced. (The actual spectrum was produced to the meeting for inspection).

Note III. *in addition to the foregoing Paper.*

Account of a Process for rendering visible the Calorific Spectrum by its effect on Paper properly prepared, and of some further results obtained respecting the distribution of Heat therein.

Received March 12,—Read March 12, 1840.

130. It is well known to artists in water colours, that their tints, when freshly laid on and wet, are deeper and darker than they ultimately become on drying, a change which must be allowed for in the colouring, or the effect will be spoiled. This is re-

marked in some colours more than in others, and is particularly striking in the case of Indian ink. It depends obviously upon the water wherewith the colours are mixed, rendering, by its refractive power, the paper beneath more penetrable by the incident light, which entering its pores becomes absorbed and lost by numberless partial reflexions.

131. If a paper so over-coloured be dried unequally, those parts which are dry first appear lighter than the rest; and if a heated body be applied at any point behind the paper while wet, the increased evaporation at the points of contact will speedily effect the appearance of a white spot or figure, tracing out the form of the body, or the locus of incident heat where radiant from it; and thus the effects of either conducted or radiant heat may be rendered sensible to the eye. It is of this property, traced a little further into its mode of operation, and exalted by certain processes, which I am about to describe, that advantage may be taken to afford a visible picture of the thermic spectrum.

132. The paper best adapted of any which I have tried for placing in distinct evidence the calorific spectrum, is that called thin post, of the thinnest kind which will bear ink-writing, such as is sold for foreign correspondence. Its thickness, measured by the sphærometer, is 0·00136 inch. One side of this paper is to be blackened with Indian ink, or, which is better, smoked in the flame of oil of turpentine, or over a candle burning with a smoky flame, by drawing it often and quickly through the flame, giving it time to cool between each exposure, till it is coated on the under side with a film of deposited black, as nearly uniform as possible. A slip of the paper so prepared is to be stretched on a frame adjusted to the spectrum-apparatus described in the foregoing pages, so as to present its white side to the incident spectrum, keeping the blackened side hollow to admit air, and to avoid rubbing off the black coat*. A fiducial dot being made on it, and brought to coincidence with the standard yellow ray of the spectrum, a flat brush, equal in breadth to the paper, dipped in good rectified spirit of wine, is to be passed over the white surface till the paper is completely saturated, which will be indicated by its acquiring a uniform blackness in place of the white it at first exhibited. After a few moments' exposure, a whitish spot begins to appear considerably below the extreme red end of the luminous spectrum, (supposing the violet end uppermost,) which increases rapidly in breadth until it equals the breadth of the luminous spectrum, and even somewhat surpasses it; and in length, till it forms a long appendage exterior to the spectrum, and extends moreover within it up to and beyond the fiducial yellow. In this state, and just as the general drying of the paper begins, by whitening the whole surface, to confuse the appearances, a second, sudden, and copious wash of alcohol from above downwards must be applied without disturbing the spectrum, or in any way shaking the apparatus. The super-

* The effect is more marked if the black side be turned to the incident rays, and the white side be viewed from behind, by using an open frame. But in this mode of observing, a strong light must be thrown on the white side, to enable the spectator to see and measure the effect; and at the same moment the spectrum must be intercepted, which is inconvenient unless an assistant be present.

fluous alcohol will have hardly run off, when the phenomena of the thermic spectrum begin to appear in all their characters, at first faintly, and, as it were, sketched in by a dimness and dullness of the otherwise shining and reflective surface of the wetted paper; but this is speedily exchanged for a perfect whiteness, marking, by a clear and sharp outline, the lateral extent of the calorific rays, and by due gradations of intensity, in a longitudinal direction, their law or scale of distribution, both within and without the luminous spectrum.

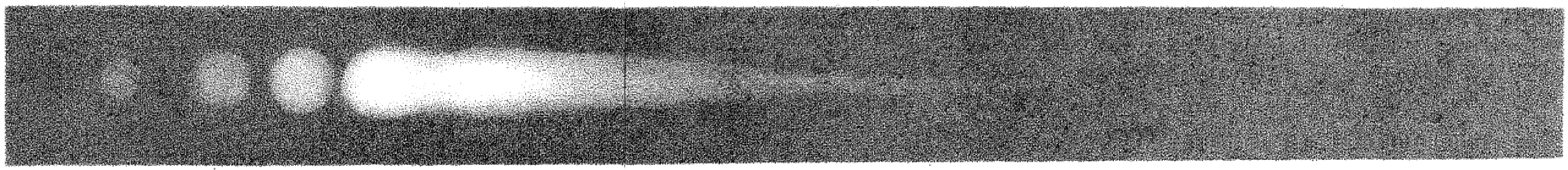
133. It may appear at first sight as if the process above described for the preparation of the paper were not in exact accordance with the principle of action at first explained. But a little consideration will show, that, as a coloured paper dries, it is the *pile* or projecting filaments which the film of moisture retreating into the paper lays bare, which first catch and reflect the light. By transferring the colour to the *under* side of thin paper, we in effect only provide for the regular and copious exhibition of such reflective filaments, unsullied by the application of colouring matter. The rationale of this will be obvious on trying a few experiments on papers coloured through their whole substance, of which the best tints are blue, and that kind of greenish brown which is in very common use among bookbinders; and the best texture a soft and bibulous one, into which liquids readily sink, and form very dark spots while wet.

134. The kind of paper is by no means indifferent in another and very important respect. It is with thermographic as with photographic papers; each has its peculiar *scale of action*. Each absorbs in preference some above others of the thermic rays, and thereby gives an undue preponderance of effect to those so preferred. It is therefore only by trials on a great variety of papers that we can satisfy ourselves whether any observed interruptions or deficiencies in the thermic spectrum be really due to the absence of calorific rays of corresponding refrangibility in the incident beam, or be not simply owing to partial insensibility in the particular paper used. The smoked paper I have above recommended seems to be more free than any other I have tried from this defect. That prepared with Indian ink is materially less sensitive, both to the most and least refracted heat-rays. In this respect, the smoked compared with the inked paper holds the same sort of relation as the bromuretted paper compared with a merely nitrated one, in respect of the chemical action.

135. Supposing, then, (unless where the contrary is expressed,) that such smoked paper is employed, the thermograph of the spectrum in its most complete state, or rather in that succession of states in which each part comes most characteristically into view, is as represented in Plate II. fig. 2, where the dimensions are enlarged in the ratio of three to two above those actually measured. On the same enlarged scale, fig. 3. represents the luminous spectrum as seen with the naked eye, and fig. 4. as seen through the standard cobalt-glass used in the above-recited experiments; while fig. 5. (still on the same scale) represents the photographic spectrum impressed on bromuretted paper*; and

* See Art. 77.

Fig. 2.



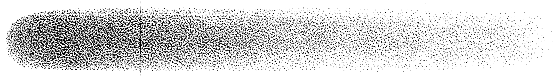


Fig. 3.

Scale of Parts.

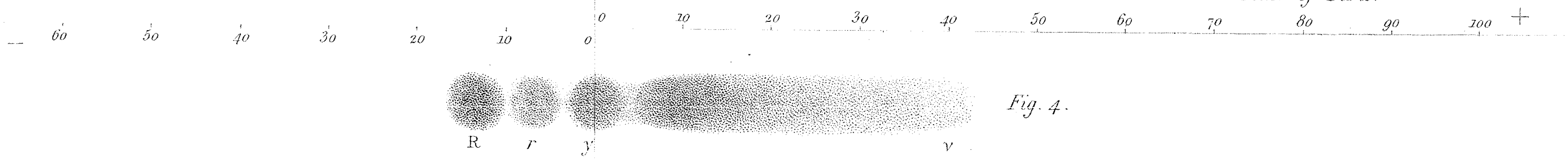


Fig. 4.

Fig. 5.

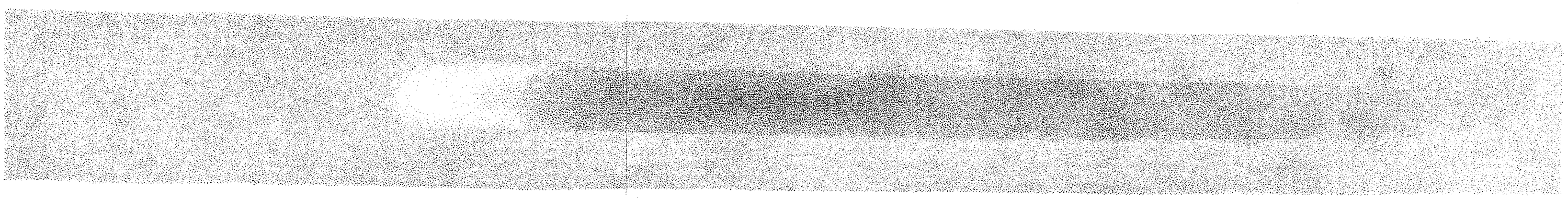


Fig. 6.

Js Basire sc.

(in order to show the greatest extent to which I have observed the whitening or conservative action of the less refrangible chemical rays to extend, and that only in one and a very peculiar case,) fig. 6. exhibits a spectrum photographically impressed on paper (No. 610.) originally prepared with successive washes of nitrate of lead, muriate of soda, and nitrate of silver, but kept for some time (five months), and thereby much impaired in point of sensibility. The same paper fresh prepared exhibits no such anomalous spectrum.

136. The most singular and striking phenomenon exhibited in the thermic spectrum thus visibly impressed, is its want of continuity. It obviously consists of several distinct patches, of which α, β are the most conspicuous and intense, but are less distinctly separated, and of which when the sun is very strong and clear it is even difficult to trace the separation. The spot γ, on the other hand, is round and well insulated. It begins to appear on the paper soon after the ovals α, β are fully formed, and when β has assumed a sharply rounded outline. The first symptom of its appearance is the dulling of the wet and shining surface of the paper, which is speedily followed by the appearance of a small round white speck; this continues to increase rapidly in size and whiteness, and at length assumes a definite and perfectly circular outline, within which the paper is entirely white. By degrees the oval β and this spot join and run together, forming a white streak deeply indented at the point of junction. It is not till this happens that similar symptoms begin to betray the existence of a still more remote heat-spot δ. Indeed, it generally requires another wash of alcohol before this can be fully brought into evidence. It is, however, perfectly unequivocal, though very much feebler, and rather worse defined than γ, with which also it is somewhat better connected than γ with β.

137. The mean of a great number of measures, as precise as the nature of the observation admits, gives for the situation of the centres or maxima of these spots, or their coordinates along the axis of the spectrum, reckoning as usual from the fiducial yellow, as follows:

α — 17·5, 19·0, 18·5, 16·0, 19, 19, 20, 18, 19, 20, 20, 19, 16, 16, 16, 18·5, 18·3. Mean of all = — 18·2.

β — 26·0, 27·5, 29·0, 25·0, 25·5, 27·3. Mean — 26·7.

γ — 36·0, 35, 35, 34·5, 36, 36, 35·5, 36, 36, 36, 36, 36·5, 37·2, 35·5, 36·5, 36·0, 35·0, 36·2, 36·0, 35·5, 36·5. Mean — 35·7.

δ — 45, 46, 46·5, 45·0, 44·2, 44·3, 44·5, 46, 44, 45·8, 45·5. Mean — 45·1.

The measures for α and β differ a good deal *inter se*, partly from the less definite nature of the maxima, and partly from having used in the measures a variety of different sorts of paper, which influence the extent and intensity of the spots α and β materially. The measures of γ and δ are closer by reason of the definite nature of the rays which respectively go to form them. Nor does the nature of the paper used in any respect displace these two spots, though it influences to a great extent their apparent intensity, and in some cases obliterates them. Indeed some coloured papers refuse to exhibit any thermographic impress whatever.

138. Of the existence of a much more remote spot I have hardly a doubt; but it is very difficult to obtain a sight of it. Its place is at or about — 55, as measured on the first occasion, when it appeared with sufficient distinctness to be set down as a positive observation, at the same time that the spot δ was placed by a similar measure at — 45·2. On another occasion (March 8), the sun being superbly clear, four measures, considered at the time quite satisfactory, were obtained of it, the mean of which was — 63·1 ; but this requires a correction for the position of the prism, which on this occasion was somewhat different from that which it had in previous experiments, it having been adjusted so as to throw the spectrum higher on the frame than before, for the sake of allowing plenty of room for the exhibition of the phænomena in question. But as on this occasion very numerous measures were also taken of the other spots, there are fortunately abundant data for calculating and applying the correction in question. I therefore set down all the measures so taken in the following Table.

Coord. of spot	α	β	γ	δ	ϵ
	— 23·0	— 28·0	— 38·5	— 48·4	— 62·7
	21·5	31·5	41·0	46·4	62·7
	19·0	31·8	41·5	49·0	63·0
	19·0	29·0	38·3	49·5	64·0
		29·5	39·5	50·0	
		30·2	40·0	50·4	
		33·0	41·5	50·5	
			41·0	49·0	
			40·0	48·8	
				50·0	
				51·0	
				51·0	
				50·2	
				50·0	
				52·0	
Means	— 20·6	— 30·4	— 40·2	— 49·7	— 63·1

If these numbers be now all reduced in the proportion of 40·2 to 35·7, so as to bring the spot γ, which is the best-defined of any, to correspondence with the former results, we have for the successive coordinates as follows:

α	β	γ	δ	ϵ
— 18·2	— 27·0	— 35·7	— 44·1	— 56·0

139. Whether these measures be considered or not as definitively establishing the existence of the spot ϵ, the equality of distribution of them all along the axis of the spectrum is not a little remarkable, and would at first sight (from the analogy of the absorptive action of nitrous gas on the luminous rays) seem to point rather to a

gaseous than a vitreous absorption as their origin. As I have no reason for preferring one to the other set of results, I shall take a mean of the two sets, which, with the differences of the coordinates or intervals between the centres of the spots, run as follows:

	Coordinates.	Differences.
Spot α....	$-18{\cdot}20$	
β....	$-26{\cdot}85$	8·65 } Mean 8·80
γ....	$-35{\cdot}70$	8·65 } Mean 8·80
δ....	$-44{\cdot}60$	8·90 } Mean 8·80
ϵ....	$-55{\cdot}50$	10·90

If we now consider that the half of 18·2 is 9·1, we might almost be led to expect a subdivision of the spot α, with its train*, into others, one of which should have its maximum at the fiducial point Y, and another half-way between that point and α. And though I am not disposed to attribute much weight to the fact, it is right to mention that when paper prepared with Indian ink was used, and a very pale yellow glass interposed between the lens and the spectrum, an oval spot, having its centre precisely on the point Y, *was* actually insulated. And this experiment, it should also in justice be mentioned, was made prior to the assemblage and reduction of the above measures, and in the absence of any speculative views concerning them.

140. The gaseous media through which the rays have reached their point of action, are the atmospheres of the sun and earth. The effect of the former is beyond our control, unless we could carry our experiments to such a point of delicacy as to operate separately on rays emanating from the centre and borders of the sun's disc. That of the earth's, though it cannot be eliminated any more than in the case of the sun's, may yet be varied to a considerable extent by experiments made at great elevations and under a vertical sun, and compared with others where the sun is more oblique, the situation lower, and the atmospheric pressure of a temporarily high amount. Should it be found that this cause is in reality concerned in the production of the spots, we should see reason to believe that a large portion of solar heat never reaches the earth's surface, and that what is incident on the summits of lofty mountains differs not only in quantity, but also in *quality*, from what the plains receive.

141. The solid media traversed by the rays in our experiments above related, are crown- and flint-glass, the latter of two varieties, though most probably differing little in composition, viz. that of which the prism and the concave lens of the object-glass are formed. On substituting a crown- for the flint-prism, the spot γ was insulated as before, but α and β were less evidently separated. When the achromatic lens was suppressed, and (still using the crown-prism) a very thin double convex crown-lens, of nearly equal focal length, was used to collect the rays, so as to get rid of flint-glass altogether, the insulation of γ was much less sensible, and the separation of α and β hardly to be perceived. This would go to point out the flint-glass as the origin of

* See Plate II. fig. 2.

the spots, and to that idea I rather incline. But the spectrum is so much contracted in length when a crown-prism is used, that it is not easy to say with certainty how far the apparent obliteration of the separating minima might be attributable to that cause.

142. When the spectrum formed by the flint-prism and achromatic lens, as usual, was displaced laterally by refraction through the thick part of a crown-prism, but little alteration took place in the relative intensities of α, β, and γ, which experiment, so far as it goes, corroborates the conclusion of the last paragraph.

143. A very different result was obtained by substituting a water-prism. The spot γ was greatly enfeebled by this, nor could δ be traced at all. The scale of transcalescence of water, therefore, would appear to be considerably more contracted than that of either flint- or crown-glass. And the same conclusion was arrived at by interposing between the lens and its focus a parallel-sided box of plate-glass. It having been first ascertained that the box when empty allowed all the spots, α, β, γ, δ, to pass freely, it was filled with distilled water, which completely destroyed both γ and δ; and so far curtailed β, that it could no longer be recognised as distinct, the thermic action being terminated at -24 by a sharp and well-defined oval outline. The upper portion of the thermic spectrum, extending above the yellow into the green and blue rays, was not attacked. That the spot γ was produced when a water *prism* was used, must be attributed to the thinness of that medium at the edge. When the box was used all the rays had to pass through 1·4 inch of water, that being the interior interval between the transmitting surfaces.

144. When muriate of lime (a saturated solution) was substituted for water, the result was nearly as with pure water, the action being cut off at -26, but not quite so sharply. I ought also to notice that it was in this experiment that the first suspicion of the existence of ε was suggested, by which it might seem that the absorptive action of this medium relaxes for the extreme thermic rays. Nitrate of silver (specific gravity 1·200) and nitrate of lead gave the same results as water. The sides of my glass box being united with a resinous cement, I could not try the effect of alcohol, ether, essential oils, &c.; nor has time permitted any further extension of the inquiry in this direction. Colourless quartz transmits α, β, and γ freely.

145. Green glasses cut off nearly the whole thermic spectrum. The oval outline of β, which passes between β and γ, as also the spot γ itself, may, however, be traced. A standard red combination, which insulated the extreme red by the joint action of a cobalt-blue and a dark brown glass, cuts off both γ and δ, and reduces the thermic spectrum to two white spots, α and β, of which the latter is greatly enfeebled. The upper edge of the spot α (which is greatly curtailed in both directions) somewhat overlaps the lower edge of the red image of the sun formed by this glass. All the more refrangible thermic rays are cut off by this combination, as they are by a cobalt-glass used singly, which latter, however, allows γ to pass freely enough.

146. A brown glass of moderate intensity transmitted α, β, and γ, the latter copi-

ously, and β more so than α; its scale of transcalescence is therefore in analogy with its colour. It has been already mentioned that a pale yellow glass insulated a spot coincident with the fiducial point Y. A solution of muriate of chromium transmitted α and β, the former most copiously, but stopped the rest.

147. In the mode of observation above described the thermic spectrum is rendered only transiently visible; ample time, indeed, is afforded for all needful measurements, and for any examination, however minute; but it seemed desirable to obtain a permanent impression or a *fixed thermograph,* capable of being preserved as a record. In this I have been to a certain extent successful, and I doubt not shall very speedily be enabled to accomplish completely this desirable object. The method which I have hitherto found to succeed best, is to dissolve in the alcohol used for washing the paper a small portion of some colouring matter, which being deposited in the pores of the paper at those points where the evaporation goes on most rapidly, in greater quantity than where it proceeds slowly, becomes accumulated on those points by successive washes to such an amount as to indicate by a marked difference of colour the distribution of the calorific rays. The colouring matter of the *Viola tricolor* is very well adapted for this purpose, as it does not develop its colour from the alcoholic tincture immediately, but requires time for oxidation, so that the experiment is not interfered with by the paper being discoloured while exposed to the spectrum.

148. To exhibit the polarization of solar heat, the following method was employed. In place of the prism, a plate of glass inclined at the polarizing angle to the axis of the lens was substituted, and intermediate between the lens and its focus a glass plate, also inclined to its axis at that angle, but in a plane at right angles to that of the first reflexion, was adapted. The focus, after reflexion at this plate, was received on prepared paper, when it formed a faint image, which of course would have been invisible were all the rays *completely* polarized. As it was, it proved too feeble to act thermographically on the paper when wetted with alcohol, thereby showing that no appreciable quantity of heat had undergone reflexion; in other words, that the thermic as well as luminous rays had received the polarized character. A plate of mica was now interposed between the lens and the first glass-plate, so inclined as to polarize at an angle of 45° a considerable portion of the reflected beam, and thereby render it susceptible of reflexion at the second glass-plate. And it was now found that the focal image, which in this arrangement was considerably bright, had acquired the power of imprinting itself thermographically on the paper, and leaving there a well-defined circular white spot. The same effect was obtained when an unannealed glass disc was used to disturb the polarity of the cone of rays.

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