XXXIV.—*On the Application of the Optical Properties of Bodies to the Detection and Discrimination of Organic Substances.*

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The optical properties of bodies, properly speaking, include every phenomenon in which ponderable matter is related to light by virtue of its molecular constitution, and not merely of its external form. Many of these, however, are of no use in helping us to follow a particular substance through mixtures or solutions containing it, though they may be useful as additional characters of substances which have been obtained in a state of isolation. Take for example refractive power. The refractive power of a pure substance, like its specific gravity, is one of the characters, the assemblage of which serves to distinguish it from other bodies; but as all bodies in nature refract light, solvents and body dissolved alike, though not to the same extent, the observation of the refractive power of a mixture would not help us in disentangling its constituents. The same may be said of dispersive power.

Circular polarization again belongs to the same class of properties; though from the fact that all inorganic, and a number of organic solvents are destitute of it, it is sometimes employed to trace a substance, but of course only in those cases in which we know or may presume that there is but one substance present which possesses the property in any marked degree.

If we exclude the emission of definite rays by flames and electric discharges, which is made known by spectral analysis, and which, though most valuable for the detection of elementary bodies, is of little or no avail for even the simplest and most stable compounds, and cannot of course be applied to organic analysis, there remain three phenomena in which bodies are related to light in a manner varying from one ray to another, not in a gradual, regular way like the refractive index, but in a way depending on something in the molecular constitution of the particular body in question, and changing sometimes in an apparently capricious way from one ray to another. These are (1) absorption, (2) fluorescence, (3) coloured reflexion.

I. The colour of substances has long been used as an important character; thus for example it is a character of the salts of oxide of copper, to yield in general blue solutions. In all cases in which colour is presented to us, we must, in considering the physical cause of the phenomenon, revert, in the first instance, to Newton's discovery of the compound nature of white light, and inquire how it comes to pass, that the homogeneous constituents of white light are presented to us in different proportions from those in which they occur in white light itself. Now, if a coloured solution be examined in homogeneous light of any kind, *i. e.*, light of definite refrangibility, it is found that the transmitted light, retaining all the properties of the incident light,* becomes feebler and feebler, as the thickness of the stratum through which it passes is increased. A portion of the incident light continually disappears as the rays traverse the solution, and is said to be *absorbed*. The incident light being by hypothesis homogenous, and the quantity of light which is absorbed in passing across a given stratum being, as

* Sir David Brewster indeed conceived that he had succeeded in analyzing by absorption light which was homogeneous as regards refrangibility. But though the direct judgment of the senses, *when the experiment is made in Sir David Brewster's manner*, is in accordance with his statement, as might be expected from his well known accuracy, the inference that a real analysis has taken place may be considered to have been disproved by subsequent researches.

experiment shows, proportional to the quantity which falls upon it, it readily follows, that the intensity of the light which escapes absorption decreases in geometrical progression, as the length of path of the rays within the solution increases in arithmetical. The rate of absorption changes in general from one set of homogeneous rays to another. For one part of the spectrum, the absorption produced by the solution may be very powerful, for another part very weak, while for another part again the solution may be sensibly transparent like water.

To determine the absolute rate of absorption for homogeneous light of a given kind would be useless, unless the body to be examined were isolated; for not only would foreign substances present contribute to the observed absorption, unless, indeed, they happened to be perfectly transparent with respect to the part of the spectrum selected, but even in an otherwise colourless solution, it would be neccessary to estimate the quantity of substance present, since the rate of absorption would depend on the strength of the solution. Hence, *absolute* absorbing power is of no more avail for our purpose than refractive power.

But the *relative* absorption of different parts of the spectrum is what may be observed at a glance (of course, qualitatively only, not quantitatively); it is in general independent of the degree of dilution of the solution, the solvents being supposed colourless, and *when the substance to be observed has in this respect well marked characters,* may be observed to a very great extent independently of coloured impurities, even though they may be sufficient to change the colour very greatly.

For this purpose, nothing more is required than to form in any manner a pure spectrum, and interpose the coloured solution anywhere in the path of the rays forming it. The simplest mode of obtaining a pure spectrum, when we have no occasion to place objects in it, is to view a slit held against a luminous background, through a prism applied to the eye. Hence the following simple arrangement may be adopted.

A small prism is to be chosen, which may be made of rather dense flint glass ground to an angle of about 60°, and need not be larger than is sufficient just to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and of laying it down on an end, so as not to scratch or dirty the faces. This forms the only apparatus required beyond what the observer may readily make

for himself. The slit may conveniently be made by taking a board 6 inches square, or a little longer in a horizontal direction, making an oblong aperture in it in a vertical direction, and adapting to the aperture two pieces of thin metal to form clean cheeks to the slit. One of the metal pieces should be moveable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinizing one part after another it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. The use of a prism in this way is at the first moment a little puzzling, but soon becomes perfectly easy. To observe the absorption-spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye; but for actual work this is an unnecessary luxury. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding to a thickness of the solution, which increases in a continuous manner from the edge of the wedge, where it vanishes.

In many cases nothing is observed, beyond a general absorption of one or other end of the spectrum, or of its middle part, and the prism gives little information beyond what is got by the eye, by observing the *succession of colours* produced by different thicknesses of the liquid. And here it may be remarked in passing, with reference to the description of pure substances, that in specifying only one colour, that corresponding to a considerable thickness, as is commonly done by chemists, the peculiar features of the absorption are left almost wholly undescribed. Thus of two solutions, one might be pink when dilute, passing on to red with increase of strength or thickness, another yellow, passing through orange to red. These would commonly be described as red, yet the series of tints indicates an utter difference in the mode of absorption, the middle of the spectrum in the one case, and the most refrangible end in the other, being the most powerfully attacked.

But in some cases, especially with substances of intense colorific power, the mode of absorption is eminently characteristic. Two or more dark bands are seen in the spectrum, indicating maxima of absorption; and the positions of these bands, their relative intensity, and their other features, form altogether a series of characters the distinctive nature of which is such as those who have neglected the use of the prism have little conception of. They render it perfectly easy in many cases to follow a particular substance among a host of impurities. For each coloured substance produces its own absorption, independently of the others (supposing the substances do not chemically react on each other), so that, unless the part of the spectrum in which the distinctive bands, or most of them, occur, is wholly absorbed by the impurities, the presence of the substance can still be recognised. Such a complete obliteration is the less likely to occur, for this reason, that when the characters of the solution are so strongly marked, it almost always happens that a comparatively small quantity of the substance suffices to produce the effect, and the solution must consequently be so much diluted that the effect of the impurities comparatively disappears.

Nor is this all. When a substance exhibits marked characters of one kind in one solvent, it often happens that it shows different and no less marked characters in a solvent of a different nature. Not only does this furnish additional characters by which the substance can be distinguished from others, but it is valuable for following the substance when involved in impurities; for the nature

of the impurities may be such as to mask the substance in one solvent and not in another. This is especially the case where one solvent is alkaline and the other acid; but differences are sometimes observed even with two neutral solvents.

To illustrate these principles, we may refer to the colouring matters of madder. Alizarin and purpurin both yield highly distinctive spectra, the former, however, only in the case of solutions containing caustic alkali,* whereas most solutions, of the latter are highly distinctive. Madder itself contains, either directly or as the result of decomposition, a number of substances which in alkaline solution absorb that part of the spectrum in which the distinctive bands of purpurin occur. Hence, in a mixture obtained from madder, and containing, we will suppose, purpurin in comparatively small quantity, the presence of purpurin would be masked by the other substances *in an alkaline solution.* But in ether or acidulated alcohol, the other substances yield spectra showing nothing particular, and interfering comparatively little with the distinctive bands of purpurin; while in an alum-liquor solution made by boiling, not only are the purpurin-bands, which in this solvent occur at a lower refrangibility than with ether, more effectually separated from the absorption produced by the associated substances, but those substances themselves are also in good measure excluded.

For an example of the necessity of attending to the nature of the solvent, even in the case of different neutral solvents, we may refer to a yellow substance which is one of the constituents of the green colouring matter of leaves. The alcoholic solution of this substance exhibits two characteristic bands of absorption, the first of which is situated immediately adjacent to the line F on the more refrangible side. The solution in bisulphide of carbon exhibits two similar bands, but much less refrangible, the line F now nearly bisecting the bright interval between the first and second dark bands. The substance is very easily decomposed by acids, and even by acid salts, yielding a product of decomposition which, in alcoholic solution, exhibits two bands of absorption like the parent substance, but a good deal more refrangible. There is the same change of position as in the former case, in passing from

* On boiling with an alkaline carbonate the same spectrum is obtained, but not perfectly developed. An alcoholic solution with a little caustic potash introduced gives it in perfection.

alcohol to bisulphide of carbon, so that the solution of the product of decomposition in bisulphide of carbon agrees almost exactly, in colour and spectrum, with that of the parent substance in alcohol.

Not only is an examination of the absorption-spectrum of a substance useful for enabling us to follow the substance through mixed solutions, but it sometimes reveals relationships in cases in which they might not be suspected, if the origin of the substances were unknown. Thus, the purpureïn of Dr. Stenhouse dissolves in ether or acidulated alcohol with a red colour, while that of the same solutions of purpurin is yellow. But the prism reveals in both cases alike the existence of three bands of absorption, of similar breadth, while the purpureïn bands are situated nearer the red than those of purpurin, by about one interval. This example shows how deeply seated in the molecular constitution of a body may in some cases be the cause which produces the bands.

Hitherto it has been supposed that the peculiarities of absorption of a substance were known, and applied to the detection of that substance in a mixture. But the question may arise:—Given a mixture of an unknown number of unknown substances, which as a whole presents peculiarities of absorption, to determine whether the whole of these peculiarities are due to the same substance, and if not, what portion are due to one substance, and what portion to another. Little can be done towards the solution of this problem by the mere observation of absorption; we can only say, that some modes of grouping of bands of absorption are common in solutions of pure substances, while others are uncommon, and give rise to the suspicion of a mixture. The phenomena of fluorescence give in some cases material assistance; but in general it is only by combining spectral analysis with processes of chemical separation, especially fractional separation, that a satisfactory conclusion can be arrived at. When a mixture is thus tested in various ways, a conviction, at last approaching certainty, is gradually arrived at, that those bands of absorption which are always found accompanying one another belong to one and the same substance.

For convenience and rapidity of manipulation, especially in the examination of very minute quantities, there is no method of separation equal to that of partition between solvents which separate after agitation. Ether combined with water, either pure or rendered acid or alkaline, is the most generally useful, and the

separation, if not otherwise fractional, may be rendered so by introducing the acid or alkali by minute quantities at a time; but other solvents are useful in particular cases. Bisulphide of carbon in conjunction with alcohol enabled the lecturer to disentangle the coloured substances which are mixed together in the green colouring matter of leaves. Solutions of various metallic oxides which are naturally precipitable by an alkali or alkaline carbonate, but are retained in solution by means of a tartrate, are very useful in the examination of the true colouring matters, not merely for producing changes of colour and spectrum without precipitation, but even, in conjunction with ether, for effecting chemical separations; and fractional separation may be effected by making the solution deviate very slightly from perfect neutrality. By combining with ether such a solution of alumina, it was found possible to separate and detect the purpurin, alizarin, and rubiacin present in a portion of powder not exceeding in bulk a fraction of the head of a pin.

II. The phenomenon of fluorescence consists in this, that certain substances in solution, or even in the solid state, when exposed to rays of one kind, emit for the time being rays of another kind, as if they were self-luminous. The following law appears to be universal:—*The emitted rays are of lower refrangibility than the exciting rays.*—The light emitted is heterogeneous, even though the active rays be homogeneous, and it is remarkable that it shows no traces of its parentage.

When a solution of a pure fluorescent substance is examined in a pure spectrum formed in the usual way by means of sunlight, it is found that, in passing in the direction from the red to the violet, the fluorescence begins with more or less abruptness at a certain part of the spectrum varying from one substance to another, and continues from thence onwards, though often with considerable fluctuations of intensity. These fluctuations are found to correspond with fluctuations in transparency, so that, in a region of the spectrum where a band of absorption occurs, the fluorescence is unusually strong, while the rays exciting fluorescence are more quickly spent, and accordingly the fluorescence does not extend so far into the solution. Experience shows that with solutions of *a pure substance*, the tint of the fluorescent light is almost perfectly constant throughout the spectrum.

In consequence of this law, the tint of the fluorescent light

emitted by a solution becomes a character of importance. This tint, it must be remembered, is that of the light *as emitted*, not as *subsequently modified* by absorption on the part of the solution, in case the solution be sensibly coloured, and some precautions are required in order to observe it correctly.* The fluorescence observed in solutions from the barks of the horse-chestnut, ash, &c., was formerly attributed indiscriminately to the presence of æsculin, whereas a purified solution from the bark of the horse-chestnut exhibits a fluorescence very sensibly different from that of æsculin, which observation alone would suffice to show that the bark must contain some other fluorescent substance besides æsculin.

As in the case of absorption, the nature of the solvent must be attended to. The colour of the fluorescent light is liable to change, not merely in passing from an alkaline to a neutral or acid solution, but even occasionally in passing from one neutral solvent to another. The lecturer has received from Dr. Müller a specimen of a substance which in water exhibits a *green*, but in ether a *blue* fluorescence.

The composition of fluorescent light, as revealed by the prism, occasionally presents peculiarities, but in such cases they are found to be connected with peculiarities in the mode of absorption, so that the two are not to be regarded as *independent* characters of a substance; and as the peculiarities in the absorption are, as a general rule, the more easily observed, it is only rarely that the analysis of the fluorescent light is of much use.

The distribution of fluorescence in the spectrum often affords valuable information, but its observation is not of that perfectly simple character, requiring hardly any apparatus, that constitutes one great advantage, for chemical application, of the observation of absorption or of the tint of fluorescent light. The observation is restricted to times when the sun is shining pretty steadily (unless the observer has recourse to electric light, or at least lime-light); it is requisite to reflect the sun's light horizontally, without which the observation would be most troublesome; and unless the reflexion be made by the mirror of a heliostat, the continual change in the direction of the reflected light is most inconvenient. It is requisite to use at least one good prism, better two or three, which must be of tolerable size, in order to have light of sufficient

* See Quarterly Journal of the Chemical Society, vol. xi, p. 19.

intensity, and the prisms must be combined with a lens, which need not however be achromatic. Hence these observations are not, like the former, adapted to the daily use of every chemist.

It has already been stated, as the result of experience, that the colour of the fluorescent light of a single substance is constant throughout the spectrum, or very nearly so. If, therefore, on examining a solution in a pure spectrum thus formed by projection, we find the fluorescence taking a fresh start *with a different colour*, we may be almost certain that we have to do with a mixture of two different fluorescent substances, the presence of which is thus revealed without any chemical process. If, however, the fluorescence of two fluorescent substances, which may be mixed together, begins at nearly the same point in the spectrum (as commonly happens when there is merely a slight difference of tint in the colour of the fluorescent light of the two substances), the coexistence of the two substances may escape detection when the mixed solution is merely examined in a pure spectrum; and in such cases a combination of processes of fractional separation with the easy observation of the tint of the fluorescent light is more searching. This is the case, for instance, with the mixture of æsculin and fraxin contained in a solution from the bark of the horse-chestnut.

Experience has also indicated a most intimate connexion between the spectral distribution of fluorescence and that of opacity in the case of solutions of pure substances. There are, indeed, theoretical reasons for regarding it as not improbable that instances may yet be found in which absorption, unaccompanied by fluorescence, takes place, in the case of solutions of fluorescent substances, in that part of the visible spectrum which is less refrangible than the point at which the fluorescence commences, but no such instance has yet been observed. Hence from the distribution of the fluorescence, we may infer the character of the absorption belonging to the fluorescent body. For this purpose it is best to make the solution extremely dilute, when any bands of absorption will have their positions indicated by beams of fluorescent light, while in the intermediate parts of relatively great transparency, the fluorescence, in the case of such weak solutions, is almost insensible.

As the occurrence of a decided difference of colour in the fluorescent light seen at two different parts of the spectrum implies, almost to a certainty, the presence of two different fluores-

cent substances, so, conversely, the exhibition of the same colour is an argument in favour of the identity of the substance producing the fluorescence at the two parts. We cannot indeed say that there may not be two substances present, the fluorescence of which commences at nearly the same part of the spectrum; but assuredly, two different substances, the fluorescence of which commenced at two widely different parts of the spectrum, would reveal themselves by the difference of colour. For experience shows that the refrangibility of the light emitted, at any part of the incident spectrum, by the solution of a pure substance, extends nearly up to that of the point of the incident spectrum at which the fluorescence commences, but not much beyond; and though, in passing from one pure substance to another, variations do occur in the relative brightness of the rays of less refrangibility which compose the fluorescent light, yet, on the whole, there is so close a connexion between the colour of the fluorescent light and the refrangibility of the rays by which the fluorescence is first produced, that no great variation in the one is compatible with constancy or a mere trifling variation in the other.

For an example of the application of these principles, we may refer to the green colouring matter of leaves. The alcoholic solution of this substance exhibits a lively fluorescence of a blood-red colour, and shows also a certain system of bands of absorption. Different chemists in different ways have obtained from it a yellow substance, and M. Frémy, having obtained a yellow substance by the aid of merely neutral reagents, has proved that such a substance pre-exists. The yellow solution was obtained by him in the attempt to divide the green colouring matter into a yellow and a blue; but, by using neutral reagents only, he did not get further in the direction of blue than a green of a bluer shade than at first, which he supposed to be due to the imperfection of the modes of separation. He conceived, however, that he had attained his object by dissolving chlorophyll in a mechanical mixture of ether and hydrochloric acid, the acid stratum, when the fluids separated after agitation, exhibiting a blue colour.

Now, when an alcoholic solution of chlorophyll is examined in a pure spectrum formed by sunlight, in the part of the spectrum extending from the extreme red to the junction of the green and blue the fluorescence exhibits remarkable fluctuations of intensity, corresponding precisely to the bands of absorption in the transmitted

light. The red fluorescence is extremely lively in nearly the whole of the blue and in the violet. This proves that the main absorption of these colours cannot be due to the yellow body; for the yellow substance would be either non-fluorescent, or its fluorescence would be of some shade of green or yellow. On the former supposition, the fluorescence of the chlorophyll solution in the blue and violet would be dull, and on the latter would be of some colour different from blood-red, unless the main absorption of that part of the spectrum were due to the substance producing the red fluorescence. In fact, when the yellow body is nearly isolated, it exhibits two characteristic bands of absorption in the blue, to which no fluorescence corresponds, which demonstrates that the slight red fluorescence which the solution may still exhibit is due to the remaining impurity. Hence, if the yellow body were wholly eliminated from chlorophyll, the residue, containing the substance showing the red fluorescence, would still powerfully absorb the blue and violet, and therefore could not be blue, but only a bluer green; so that in seeking to separate chlorophyll into a blue and a yellow substance, M. Frémy was aiming at an impossibility. His phyllocyanin is, in fact, a product of decomposition, and is not blue at all, but merely dissolves in certain acids with a blue colour. It may be mentioned in passing, that the green fluorescent residue is still a mixture, consisting of two different substances, both green, and both exhibiting a red fluorescence.

III. The instances in which substances appear coloured by reflexion are comparatively rare. It is very common in chemical descriptions to read of a solution appearing of such a colour by transmitted, and such a colour by reflected light. In many cases, this is a positive mistake, and the colour described as due to reflexion is really due to transmission. A chemist views a solution contained in a test tube by transmission, and then by reflexion; and seeing, perhaps, some perfectly different colour in the latter case, describes it as the colour of the solution by reflexion, whereas it is merely the colour by transmission due to a greater thickness, the light having been reflected at the back or bottom of the test tube, and so having twice passed through the solution. In other cases the colour described as due to reflexion really arises from fluorescence; and though the statement may be true in the sense intended, it seems objectionable to apply the term *reflexion* to a

process so utterly different. It is only in the case of metals, such as gold and copper, and of certain other substances such as murexide, platocyanide of magnesium, &c., that colour is really seen as the result of reflexion.

When this takes place in the case of non-metallic substances, they are found to be endowed, for the colours so reflected, with an intense opacity, comparable with that of metals; while for other parts of the spectrum they may be comparatively transparent, and these parts they reflect with an energy comparable to that of a vitreous substance only. The variations of absorbing power in passing from one part of the spectrum to another, and consequently the variations in reflecting energy, are frequently much more considerable, and accordingly the colour by reflexion is much richer than in the case of metals.

An excellent example of the intimate connexion between metallic reflexion and intense absorption is afforded by crystals of permanganate of potash. These crystals exhibit a green metallic reflexion, and when crushed yield a powder of an intense purple colour by transmitted light. The colour is too intense for spectral analysis, but the solution has a similar colour, merely less intense as corresponds with its smaller concentration, and the analysis of the light transmitted by the solution presents no difficulty. The green is quickly absorbed, but when the solution is sufficiently dilute, five eminently characteristic bands of absorption are seen in that part of the spectrum. A sixth band comes out with a greater thickness or else strength of solution, but even the fifth is somewhat less strong than the others. When the light reflected from a crystal is analysed, four bright bands are seen standing out on a generally luminous ground of inferior brightness. These bright bands correspond in position with the principal *dark* bands in the light transmitted by the solution, and therefore, it may be presumed, by the crystals themselves. When the angle of incidence has a suitable value, and the reflected light is analysed by a Nicol's prism, with its principal plane in the plane of incidence, and then by a common prism, the spectrum is reduced to these four bright bands. A fifth bright band could perhaps be made out, in the case of a fine crystal with a fresh surface. Under the circumstances described, the Nicol's prism would extinguish the light reflected from a vitreous substance, and transmit much of that reflected from a metal. We see, therefore, that, as regards its relations to light, the crystallized body passes repeatedly from

the condition of a vitreous to that of a metallic substance and back again, as the refrangibility of the rays, in relation to which it is considered, is continuously increased by a small amount.

The same relation between intense absorption and metallic reflexion exists generally, though it cannot be always studied by means of a solution. The platinocyanides, for example, yield colourless solutions, so that the intense absorption which most of them exercise for certain parts of the spectrum must be attributed to the mode in which the molecules are built up in forming the crystals; but by attending to the colour of the light transmitted by thin crystals, the law is found to be obeyed. Gold can only be obtained, in solution, as gold by means of the opaque solvent mercury; but its colour by transmission may be studied in gold leaf, or in a chemically deposited film, and is then found to be conformable to be law mentioned, the less refrangible colours, which are those which are the more copiously reflected, being also those which are the more intensely absorbed.

When a body endowed with the property of coloured reflexion, such as permanganate of potash, is dissolved, in consequence of the necessary dilution, the opacity of the medium ceases to be, for any part of the spectrum, of that intense kind which is necessary for quasi-metallic reflexion; and accordingly the light reflected by the solution is colourless. Hence coloured reflexion is not available for following a substance through mixtures containing it. The chemist ought, however, to be acquainted with its laws, in order to understand the changes of colour which a substance possessing the property is capable of exhibiting in the solid condition, according to its state of aggregation.

In order that the colour due to reflexion should appear, it is necessary that the substance should have a certain amount of coherence. Thus indigo in the form of a fine loose powder is blue, even when viewed by reflexion. It would be erroneous, however, to describe the body as blue by reflexion, if we were speaking of the properties of the substance, and not the mere crude results of observation made under given circumstances. For though it is true that the light by which the blue colour is seen has undergone reflexion (without which it would not have reached the eye) it is not *in reflexion* that the chromatic selection is made by virtue of which the powder appears blue, but *during transmission*. In fact it is only a small portion of the light that is reflected at the outer

irregular surface of the mass; the greater part penetrates a little way, and is reflected at various depths, and in passing through the particles, in going and returning, suffers absorption on the part of the coloured substance. Were the substance intensely opaque for *all* the colours of the spectrum, the powder would be not blue but black, as we see in the case of platinum-black. By burnishing, the powder is reduced to the state of a somewhat coherent mass, and it now begins to exhibit the copper colour due to reflexion. The internal reflexions are at the same time greatly weakened, so that the part of the light which is reflected from beneath and undergoes absorption is much reduced. A pressed mass is not, however, an optically homogeneous medium, so that the colour by reflexion obtained by burnishing cannot in general be quite pure. In the state of a fine crystalline powder, indigo exhibits a mixture of the copper colour due to reflexion, and the blue colour due to transmission, though observed in the light reflected from the mass as a whole; while if the substance could be obtained in large crystals, the colour by reflexion would be seen in perfection, and the colour by transmission would disappear, the crystals being sensibly opaque.