XV.—*Observations on the Origin of Colour and on Fluorescence.*

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COLOUR is an effect due to an absorption of some of the rays of light emitted by a white hot incandescent solid or by a substance in a state of incandescent vapour.

The origin of colour is the synchronism of the undulations of the emitted rays with the vibratory motions of the molecules, or the motions within the molecules, of the substance into which the rays enter, whereby the rays are absorbed (*Trans.*, 1881, **39**, 165).

Colours may be visible or invisible, but a visible colour is one which causes absorption of any rays with wave-lengths not greater than about 7951, the deep-red ray of rubidium, and not less than 3933, the more refrangible of the rays in the violet, H_1 and H_2 .

In order to study the "origin of colour," we must first consider the case of colour in those molecules which are of the simplest possible constitution, such as, for instance, the molecules of chlorine, bromine, and iodine, of oxygen, ozone, and water.

Oxygen, ozone, and water are three coloured substances; the colour of each is blue. It is the effect of definite bands of absorption which extinguish rays with wave-lengths capable of being accurately measured, and therefore representing definite periods of vibration or oscillation-frequencies. The undulations of the absorbed rays are synchronous with, and in opposite phase to, the vibrations of the molecules of the respective substances. The colour or effect on light caused by molecules of oxygen, ozone, and water is in no way different from that caused by molecules of aniline-blue. The colour of the former molecules is less strikingly visible, and their tinctorial power is feebler because the absorption bands by which it is caused are much narrower, that is to say, they are restricted to fewer radiations than the bands of absorption in aniline-blue.

It cannot therefore be correctly stated in general terms that colour is due to special forms of intramolecular structure or special modes of atomic arrangement such as can be represented by chemical formulæ, because these substances are so widely different in constitution and have very little in common (*Proc.*, 1888, No. 4, 27). The statement may, however, be applied in a restricted sense to certain carbon compounds, especially to those which contain oxygen and nitrogen, and which are essentially of the class to which organic dye-stuffs belong.

Armstrong, having been led to conceive certain conditions as

necessary for the exhibition of colour by an organic compound, has endeavoured by modifying the formulæ of various well-known substances to make their constitution conform to that which a coloured substance ought to possess according to his views (*Proc., loc. cit.*).

The condition under which he represents all coloured molecules as existing is one of strain in their structure which gives them a certain degree of instability. He employs a special sign, $\bigcirc$, to denote this strained condition; it is used in the same way as the parallel lines which indicate the double linking of carbon atoms.

The indications of a condition of strain are, I gather, as follows:—

1. Graebe and Liebermann, also Baeyer, observed that almost all organic colouring matters derive the physical property of colour from the manner in which the oxygen or nitrogen atoms are grouped, and that colouring matters are rendered yellow (converted into leuco-derivatives) or colourless by the action of reducing agents (*Ber.*, **1**, 17 and 106).

2. There is an instability and an activity characteristic of the coloured molecules of oxygen compounds of many metallic elements (*Trans.*, 1887, **51**, 154).

3. The simplest organic colour is quinone, the example cited by Graebe and Liebermann (*Ber.*, **1**, 106).

4. According to Armstrong's view, there is no instance of a hydrocarbon being coloured, if we give the term its conventional meaning.

5. Very many colouring matters have a complex constitution, and their structural formulæ may be varied to admit of them being written as substances resembling quinone.

In several cases, Dr. Armstrong alters the structural formulæ either of substances which are not coloured which he considers ought to be, or of those which are coloured, and which, according to the usual view of their constitution, do not sufficiently exhibit the condition of strain already referred to. The truth which underlies this conception of tension or strain is the fact that almost all organic colouring matters are obtained from benzenoid hydrocarbons, their derivatives or congeners; and that they contain oxygen or nitrogen or both.

Otto Witt defined a colour produced from an aromatic compound as the result of the action of a chromophore upon a chromogen, but it is not necessary to have a salt-forming group present unless the substance is to constitute a dye-stuff. Chromophores are groups of atoms as NO_2 , CO , $\text{N}=\text{N}$. For instance, azobenzene is a strongly coloured substance, but it is not a dye. I have dealt with this matter (*Trans.*, 1887, **51**, 153), and shown that a chromogen is a coloured substance, the colour of which is invisible, but that under the action of a chromophore the colour becomes modified so that it is visible.

Armstrong has stated that the paraffins are all but colourless even in the infra-red and ultra-violet regions of the spectrum, but that the unsaturated hydrocarbons begin to manifest colour in regions above and below the visible spectrum. I have found that the paraffins and their derivatives, such as alcohols and acids, absorb the ultra-violet rays, the absorption taking place at the more refrangible end of the spectrum. Moreover there is no difference to be observed between the character of the absorption shown by the paraffins and that of the unsaturated hydrocarbons of the ethylene and acetylene types.

In fact, *all open chain hydrocarbons exert a continuous absorption, the extent of which is dependent upon the number of carbon atoms in the molecule.*

All conclusions as to the origin of colour which are based upon a belief that there is any difference between the nature of the absorption of rays by the normal paraffins and the unsaturated hydrocarbons appears to me not only fallacious, but to have, in fact, no foundation whatever.

The most colourless substance known is hydrogen. That is to say, the rate of vibration of its atoms or its molecule is of all elements the most rapid. I have always attributed this fact to its mass being so much less than that of any other element, but it is probably due more to the large amount of energy that is associated with the molecule.

Hydrocarbons are the least coloured of all other carbon compounds, because the energy of the hydrogen atoms is communicated to the whole molecule. This might account for hydrogenised colouring matters becoming colourless, and, in fact, it has been shown that hydrogenised substances absorb the ultra-violet rays less powerfully than those substances from which they have been derived (Trans., 1885, 47, 693). If we compare the absorptive power of any two hydrocarbons containing the same number of carbon atoms, that containing the fewer hydrogen atoms will exert the greater absorption. Comparing C_2H_6 , C_2H_4 , and C_2H_2 , 1 mol. of the gas containing the most hydrogen will transmit the longest spectrum.

The rate of vibration of a molecule is slackened by the entrance of oxygen into its constitution, because the molecule is weighted thereby, and one or more atoms of hydrogen have been removed. This has been shown to be the case by a spectroscopic examination of the normal alcohols, and of monobasic and bibasic acids (*Phil. Trans.*, i, 160, 257).

It has been remarked that the occurrence of colour is more frequently than not concomitant with a high degree of reactivity, the coloured compound being usually of "high potential," or slight stability. If oxygen compounds such as manganates, permanganates,

chromates, and such like substances are referred to, this arises simply because they are endothermic compounds.

Oxygen is in the free state blue, as Liveing and Dewar have shown, and in the endothermic molecule, ozone, its blue colour is intensified. It is, moreover, as I have shown, fluorescent.

The condensation of the atoms of oxygen in the molecules of ozone, permanganates, chromates, &c., intensifies the colour of the compounds, and such condensation can only take place by absorption of heat, or some other form of energy measured in terms of heat.

If we consider the condensation of carbon atoms in the molecule of hydrocarbons, and of the parent substances of organic colouring matters, similar facts come into view, thus:—

CH_4 .	C_2H_4 .	C_2H_2 .	C_6H_6 (gaseous).
Exothermic.	Endothermic.	Endothermic.	Endothermic.
+18.5	—15.4	—61.1	—12
Heat units.	Heat units.	Heat units.	Heat units.

Of these none forms a visibly coloured compound, except benzene, and the compounds of benzene are not visibly coloured unless they contain nitrogen, oxygen, or both. All chromogens are endothermic, and several chromophores.

In fact, the following statement may be accepted as law:—

All organic colouring matters are endothermic compounds, or derivatives thereof.

This statement includes derivatives of benzene, triphenylmethane, naphthalene, anthracene, the tertiary bases, ferrocyanides and other cyanogen compounds, and also murexide. It explains why, according to Gräbe and Liebermann, coloured molecules are rendered colourless by reducing agents, for heat would be evolved by the action of nascent hydrogen on such substances. The rate of vibration is always increased by the addition of hydrogen, or by the removal of oxygen from a molecule, or by both causes operating simultaneously, so that absorption bands are transferred from the visible to the ultra-violet region, or are altogether destroyed. I conceive this to be the physical cause of that which Armstrong has not defined, but which he terms "reactivity" and "high potential."

I have stated in a former contribution (Trans., 1887, 51, 153) that a coloured substance is one which always absorbs rays at either end of the spectrum, or selects rays from some intermediate portion of the spectrum. "Every fluorescent substance is therefore coloured." That is to say, it exerts absorption, either continuous or selective, in some part of the ultra-violet or visible spectrum, so that, though its fluorescence may exhibit a visible colour, its colour due to absorption

may be invisible. In other words, fluorescence might be inferred to be something verging upon actual coloration if the absorbed rays extend close up to the violet region, that is to say, to about wavelength 3900. I have shown that this is the case with anthracene, and therefore Dr. Armstrong is in agreement with me when he remarks that its fluorescence is "the beginning of colour."

On the other hand, however, I cannot admit that anthracene is a colourless substance in any acceptation of the word, nor is it possible to allow that a brilliant fluorescence is an indication of incipient visible colour. My reasons are two: first, anthracene has a definite absorption band in the violet, and is therefore coloured, though its colour may be slight, and from certain causes, which I shall mention, it cannot be seen by a mere glance; secondly, many substances which show no fluorescence do not exert selective absorption, and several of those which do are not fluorescent. Many fluorescent substances exert only a continuous absorption at the more refrangible end of the ultra-violet spectrum, and have therefore nothing approaching to a visible colour.

Eight years ago, during the progress of some other work, I observed fluorescence in a great variety of substances, and although I had intended to reserve the observations then recorded for future investigation, it seems desirable that they should be made known at the present time, and I beg therefore to place them at the disposal of the Chemical Society.

Method of experimenting on Fluorescence.

The source of light was a condensed electric spark, the electrodes being prepared from lead-cadmium and tin-cadmium alloys containing 25 per cent. of cadmium. The spark apparatus was placed in a box with a circular aperture, in front of which was a quartz lens of about 6 inches focus. The rays of the spark were thus brought to a focus at about 12 to 18 inches from the lens. The whole of the experiments were made in a dark room. The liquids examined were contained in quartz cells 20 mm. in thickness. They were viewed by looking at them in a direction at right angles to the direction of the rays which passed through the middle of the liquid. In cases where the fluorescence was doubtful, the sides of the cells were screened from the eye, and precautions were otherwise taken to prevent scattering of light being mistaken for fluorescence. It is believed that an examination of the results obtained with a great variety of different substances will afford evidence that no mistake of the kind has occurred.

The Appearance of Fluorescence.

When a substance like quinine sulphate is examined, there can be no question as to the colour of the fluorescence, for it is bright enough to be observed with a spectroscope. But although many substances are strongly fluorescent, the fluorescence is not always strongly coloured. The colours observed in fluorescence have been deep red, crimson, yellow, green, blue, and violet. Sometimes a violet or blue fluorescence is barely visible, yet the fluorescence is strong, and the cell of liquid appears filled with light. This light to my vision is like the phosphorescence of phosphorus vapour, more or less yellowish or white. To this appearance there is occasionally added a bluish, greenish, or violet tinge, more or less pronounced. Hence the description of a strong fluorescence with a barely visible colour, or with no distinct colour, must be accepted as indicating a strong luminosity with feeble coloration.

It should be observed that the substances examined were at first chiefly alkaloids and their salts, and, later, acids, alcohols, and a variety of organic compounds which were selected and examined in the order given with a definite object in view.

The alkaloids were generally dissolved in alcohol of about 98 per cent., and, unless otherwise stated, this is the alcohol referred to in the notes. Sometimes acid was added to the alcohol, and this is described as $\text{H}_2\text{SO}_4/1000$, which means 98 grams of sulphuric acid per litre. Almost all the specimens of alkaloids were obtained from the actual makers for the original purpose of examining their absorption spectra, particulars of which are given in the *Phil. Trans.*

Alkaloids and Salts examined for Fluorescence.

Quinine. 0.02 gram dissolved in 20 c.c. of alcohol. Sp. gr. 0.8.

Beautiful bright violet fluorescence.

Quinine sulphate. 0.02 gram in 20 c.c. of absolute alcohol with one-fourth of its volume of $\text{H}_2\text{SO}_4/1000$. Brilliant sky-blue fluorescence.

Quinidine sulphate. 0.02 gram in 20 c.c. of alcohol with one-fourth its volume of $\text{H}_2\text{SO}_4/1000$. Blue fluorescence.

Cinchonine. 0.02 gram in 20 c.c. of alcohol. Blue fluorescence.

Cinchonine sulphate. Containing 1/1000 of base. Brilliant sky-blue fluorescence.

Cinchonidine sulphate. 0.02 gram in 20 c.c. of alcohol with one-fourth its volume of $\text{H}_2\text{SO}_4/1000$. Bright sky-blue fluorescence.

- English aconitine. 0·1 gram in 20 c.c. of alcohol. Greenish-blue fluorescence.
- Foreign aconitine (inactive). 0·1 gram in 20 c.c. of alcohol. None.
- Pseudoaconitine. Solution 1 in 1000 of alcohol. Purple fluorescence.
- Quinine hydrochloride. The quinine solution acidulated with strong hydrochloric acid. Very faint fluorescence. Colour very indistinct; rather like the vapour of phosphorus when seen in the dark.
- Hydrochloric acid. None.
- Narcotine (fresh solution). 0·02 gram in 20 c.c. of alcohol. None.
- Narcotine (an old solution). 0·1 gram in 40 c.c. of alcohol. Greenish fluorescence.
- Oxynarcotine (old solution). 0·1 gram in 25 c.c. of alcohol. Bluish fluorescence.
- Oxynarcotine (fresh solution). 1 gram in 1000 c.c. of alcohol. Bluish fluorescence.
- Narceïne. 0·1 gram in 25 c.c. of alcohol. Very indistinct blue fluorescence.
- Tetracetylmorphine. 0·1 gram in 20 c.c. of alcohol. Very faint blue fluorescence.
- Thebaïa. 0·1 gram in 20 c.c. of alcohol. None.
- Codeïa. 0·1 gram in 20 c.c. of alcohol. Very faint blue fluorescence.
- Diacetylcodeïa. 0·1 gram in 20 c.c. of alcohol. None.
- Papaverine. 0·1 gram in 40 c.c. of alcohol. Greenish-blue fluorescence.
- Cotarnine hydrobromide. 0·1 gram in 20 c.c. of alcohol. Pale greenish-blue fluorescence.
- Strychnine. 0·1 gram in 100 c.c. of alcohol. None.
- Brucine. 0·1 gram in 25 c.c. of alcohol. None.
- Japaconitine. 0·1 gram in 10 c.c. of $\text{H}_2\text{SO}_4/1000$. Blue fluorescence.
- Pipereïne. 0·1 gram in 20 c.c. of alcohol. Faint blue fluorescence.

Dyes and Coloured Substances.

The following substances are dyes :—

- Rocellin, or fast red (β -naphthol-azonaphthylsulphonic acid). Strong and weak solutions in alcohol. Absolutely non-fluorescent.

- Acid brown (α -naphthol-azonaphthylsulphonic acid). Strong solution in water not fluorescent. Very dilute solutions, lavender fluorescence.
- Helianthin. Strong solutions not fluorescent. Faintly fluorescent in weak alcoholic or aqueous solutions.
- Benzene-azo- β -naphtholdisulphonic acid. Strong solutions not fluorescent. Weak solutions exhibit a magnificent bluish-violet fluorescence.
- Amidoazo- α -naphthalene. Strong solutions not fluorescent. Magnificent greenish-blue fluorescence in weak solutions.
- Amidoazo- β -naphthalene. Magnificent bright blue fluorescence in alcoholic and aqueous solutions.
- Cumene-azo- β -naphtholdisulphonic acid. Strong solutions not fluorescent. Lavender-blue fluorescence in dilute aqueous and alcoholic solutions.
- Diphenylamine-blue. Lavender-blue fluorescence in dilute aqueous solutions.
- Magenta (rosaniline hydrochloride). Not fluorescent even in strong or dilute aqueous solutions.
- Safranine. Strong solutions not fluorescent. Brilliant reddish-yellow to yellowish-red fluorescence in very dilute aqueous solutions varying with strength.
- Magenta (rosaniline acetate). Not fluorescent in strong solution. Light-blue fluorescence in dilute solutions.

Various Substances.

- Methyl alcohol.* Prepared from very pure methyl oxalate. Very slightly bluish, but fairly strong fluorescence.
- Ethyl alcohol.* Marked fluorescence. Colour slightly blue, or bluish-violet.
- Propyl alcohol.* Slight blue fluorescence.
- Isobutyl alcohol.* None.
- Urea. 0.2 gram in 20 c.c. of water. No distinct fluorescence.
- Glucose. 0.2 gram in 20 c.c. of water. Nothing distinctly coloured, but a slight luminosity, due to fluorescence.
- Ozone. Oxygen containing 17 per cent. of the gas. Steel-blue fluorescence.
- Pure benzene. Crystallised. Bluish fluorescence.
- Azobenzene. In very dilute alcoholic solutions. Faint, greenish-blue fluorescence.

* These substances are the identical preparations described in the *Phil. Trans.* (1879, 170, 257). It is believed that no purer specimen of methyl alcohol was ever prepared.

Ether. Very carefully prepared and dried. A barely visible fluorescence. Doubtful.

Chloroform. Doubtful. Fluorescence, if any, very feeble.

Glycerine. Strong, pale-violet fluorescence.

Glacial acetic acid. Scarcely visible colour, but strong fluorescence.

Sulphuric acid. Indistinct. Barely visible, but resembling the fluorescence of quinine hydrochloride.

The bluish-violet fluorescence of alcohol and the violet fluorescence of quinine are destroyed by placing a cell containing either hydrochloric acid or chloroform in front of the cells containing alcohol or quinine.

In quinine hydrochloride, a drop of sulphuric acid develops the magnificent blue fluorescence characteristic of the acid sulphate.

Nitric acid. A barely visible fluorescence. Colour indistinct.

Volcanic ammonia. A barely visible fluorescence, less marked even than that of nitric acid. No decided colour.

Tap water. Barely visible light; no colour. Apparently slightly fluorescent.

Distilled water. Nothing decided, but a very faint light seen in cell. Fluorescence is very doubtful.

Optical glass of Chance's make.

Crown glass. Beautiful blue fluorescence. Very strong.

Light flint glass. Density, 3.2. Beautiful blue fluorescence. Strong.

Heavy flint glass. Density, 3.64. Beautiful blue fluorescence. Strong.

Heavy flint glass. Density, 3.66. Beautiful blue fluorescence. Strong.

Rock crystal. Pale bluish-violet fluorescence.

Flint glass specimen bottles, from the Whitefriars Glass Works. Beautiful bright-blue fluorescence.

The rock crystal transmitted all rays of the spectrum, from wave-length 7950 up to and including wave-length 2000, that is to say, from the red to the extreme ultra-violet. Probably the absorption which causes fluorescence lies beyond λ 2000.

These different varieties of glass are quite as brilliantly fluorescent as anthracene, or as a solution of quinine sulphate under the same illumination.

The following observations are to be noted :—

1. Quinine dissolved in alcohol exhibits a beautiful bright violet fluorescence.

2. Hydrochloric acid is not fluorescent.
3. Quinine hydrochloride is very faintly fluorescent, but without distinct colour.
4. Chloroform is feebly fluorescent, but without distinct colour.
5. Both hydrochloric acid and chloroform can cut off those rays which are the cause of the fluorescence in quinine.
6. Some of the alkaloids may be recognised by the degree and colour of the fluorescence they exhibit, as for instance the different aconitines.
7. Normal alcohols are fluorescent; so also are the fatty acids.
8. Glycerol has a violet fluorescence.
9. Benzene has a pale-blue fluorescence; azobenzene greenish-blue.
10. Rock crystal has a pale bluish-violet fluorescence, flint glass a strong blue, and crown glass a very strong and beautiful blue fluorescence.
11. Substances which are not fluorescent in strong solutions may become so on dilution. This is characteristic of those substances which exert a very powerful absorption of the ultra-violet or the visible rays.

Fluoresceine, which may easily be examined by ordinary light, is a good example of this. It powerfully absorbs those rays which cause its fluorescence, hence only in dilute solutions, when the absorption is weakened, does the fluorescence exhibit itself.

I will now advert to the fact that Dr. Armstrong assumes both quinine and quinine hydrochloride to be non-fluorescent. In view of the experiments just quoted, this appears to be erroneous. He next explains the non-fluorescence of the hydrochlorides as probably due to a splitting up of the salt, but an examination of its absorption spectrum (not published) and those of the allied bases, for instance, quinoline, hydroquinoline, tetrahydroquinoline, and their hydrochlorides, shows that this is not the case (Trans., 1885, 47, 685). The reason which I consider to be valid is the absorption by hydrochloric acid of those rays which are the cause of the fluorescence in quinine. In like manner dilute solutions of rosaniline hydrochloride are not fluorescent, whilst those of rosaniline acetate are.

In this connection, it may be well to consider the cause of fluorescence. It is the retardation of some of the rays of a beam of light during their passage through a substance, so that their rate of vibration is reduced, and the length of their waves increased. This is usually expressed by saying that the rays are lowered in refrangibility.

It will appear from the behaviour of many of the substances on the foregoing list that they may be divided into three groups:

Group 1. Substances which absorb the rays.

Group 2. Substances which retard the rays without effecting great absorption.

Group 3. Substances which absorb the rays in strong solutions, and only retard them in weak ones.

There is one substance I have not mentioned which is remarkably fluorescent, namely, unsized paper. The whole of the ultra-violet spectrum as far as wave-length 2000 is rendered visible when allowed to fall on a sheet of white blotting-paper; but this fluorescence is without distinct colour. The eye must be rendered sensitive by being in the dark for some minutes, and no stray rays of light must illuminate the paper; but so distinctly are the lines in the spectrum of cadmium made visible that they may be well focussed on such a screen. This can only be the case if the paper is fluorescent to all the rays, and that these are lowered in refrangibility.

Obviously rays of such short wave-lengths as are invisible under ordinary circumstances, because they are absorbed by the aqueous humour of the eye, could not be seen by reflection; and, if they could, a sheet of glass would render them visible when viewed at a proper angle. It must, therefore, be the case that the paper is fluorescent. As Sir George Stokes has shown, a very great variety of substances are fluorescent.

This strengthens my conclusion, that we cannot accept any general statement* which implies that fluorescence is a feeble manifestation of that which we ordinarily describe as colour.

The special instance referred to by Armstrong, namely, that of anthracene, is an exceptional one in which fluorescence is simply associated with, but not necessarily consequent upon, a definite absorption in the more refrangible rays of the visible spectrum or in the less refrangible rays of the ultra-violet.

The purest anthracene, distilled twice or thrice from an excess of caustic alkali, has been carefully examined. It shows the most brilliant fluorescence, and it has a greenish-yellow colour. When transparent crystals are seen by reflected light, they appear white with a superadded violet or bluish tint due to fluorescence. But the same crystals, viewed by transmitted light, are greenish-yellow, and the colour is more distinctly seen when the crystals are carefully melted. The colour by transmitted light is complementary to that which is absorbed. That anthracene is a substance which is not deeply coloured may be easily explained by the following facts:—

* "The origin of Colour. Note on the appearance of Colour in Quinoline derivatives and of Fluorescence in Quinine salts," *Trans.*, 1887, 51, 789.

First, the absorption band, which is the cause of the colour, is a narrow one; secondly, the absorbed rays are not powerfully luminous; thirdly, because the real colour of the substance is neutralised by the unabsorbed violet rays which are close beside the absorbed rays, and are very nearly of a complementary tint.

The colour of the fluorescence is in itself sufficient to extinguish the colour of absorption proper to anthracene.

In 1879, in conjunction with Professor Huntington, certain isomeric nitro-compounds were studied by me, but neither at that period nor since have I become aware of any evidence that compounds which in the conventional sense are coloured have of necessity a different constitution from compounds ordinarily said to be colourless. It is on that account impossible for me to adopt the hypothesis that ortho-nitrophenol is really *quinoneorthonitroxime* ("The Origin of Colour, II: The Constitution of Coloured Nitro-compounds," *Proc.*, 1892, 101) simply, and for no other reason, because it has a yellow colour, or to assume that metanitriline is not a uniform substance, or that its structure is really not that of imidonitrobenzene because its constitution is not that which, according to Armstrong's view, a yellow substance ought to have. An examination of the absorption curves of the 1:2- and 1:4-nitrophenols, figured in the *Phil. Trans.*, i, 1879, will show the close similarity of their spectra. By an error which it would not be difficult to explain, the ortho-nitrophenol has been described as para-, and *vice versa*, but, as the specimens examined are still in existence and are correctly labelled, there can be no doubt as to which of them the description is intended to apply. In Diagram 23 (*loc. cit.*), it will be seen that ortho-nitrophenol has a band of absorption extending completely through the ultra-violet into the blue rays, hence its yellow colour, whilst the absorption, caused by the paranitrophenol (Diagram 22), terminates in the violet, and the substance is therefore practically colourless. In metanitriline we have an absorption band carried as far as the middle of the violet, but in the para-compound a strong absorption band occurs in the blue. The two substances are therefore both coloured, but the latter has the deeper tint. Now, if metanitriline were not of uniform composition, then the absorption spectrum of a dilute solution would at some part of the curve afford evidence of the presence of another substance. There is no such indication to be traced in these curves, and they are, in fact, very much what one would expect to find them.

The facts referred to by Armstrong, that the metallic derivatives of paranitrophenol are coloured whilst the substance itself is colourless, is precisely what I should have predicted from its spectrum, that methoxyortho-nitrophenol is colourless whilst the parent substance is

yellow, and that the benzoate of the yellow metanitriline is colourless, are instances of several such changes which I have studied, but, at present, I am not prepared to give an account of them. There are many instances of substances being colourless which, by analogy, might be expected to be coloured. For instance, NO_2 is visibly and strongly coloured, but NO_2OH has no visible colour, its absorption being in the ultra-violet. Chlorine, bromine, and iodine, are coloured but their hydracids are not, neither are their oxygen acids, nor the salts of such acids. Nitric acid, hydriodic acid, and the haloid oxygen compounds are all endothermic substances, and why they are not coloured requires some explanation. It may, however, be remarked that in dealing with yellow substances the difference between colour and no colour is very slight. The colour may be intensely strong, but a very little shifting of the region of absorption to rays a little more or a little less refrangible than the solar rays H_1 and H_2 makes such substances as the nitrophenols and nitranilines colourless or coloured.

The general conclusions recorded in my former communications on the subject of colour and chemical constitution (*Trans.*, **39**, 153; **41**, 45; **47**, 685; **51**, 154) have been confirmed by G. Krüss and also by Schütze (*Zeit. physikal. Chem.*, **9**, 109, 1892). I refer more particularly to the raising and lowering of tint by the introduction of hydrogen on the one hand, or by the substitution of hydrocarbon radicles for hydrogen on the other; having, however, dealt with a much greater range of spectrum than later investigators, I have shown how this operates, so as to convert a colourless into a coloured substance. But in causing visible colour or in changing its tint we must consider not only the effect of mass on the chromogen but also on the chromophore, and then, as the chromogens are endothermic compounds, it is necessary, also, to take into account the energy of the molecule or atomic grouping which, while entering into them, varies their tint.

That there are certain structural formulæ which are common to many strongly coloured dyes admits of no question, and from the result of many observations I should be led to expect the most powerfully tinctorial property to belong to those substances with formulæ which indicate the highest endothermic values for the chromophores, the nucleus being a closed chain compound such as benzene, for instance, with an invisibly coloured chromogen.

During a protracted and systematic study of absorption spectra of inorganic and organic substances, I have endeavoured to elucidate the cause of the production of coloured derivatives from what are ordinarily termed colourless hydrocarbons, and no one is more unlikely to fail in appreciating every attempt made, both by reasoning

and experiment, to discover something in their constitution common to all substances which are visibly coloured.

It is, however, impossible to dissociate the phenomena exhibited by hydrocarbons in the ultra-violet part of the spectrum from identical phenomena exhibited by their derivatives in another part of the spectrum ; still less is it possible to dissociate the phenomena which produce the narrow bands of absorption in the spectrum of water from those which are the cause of the broad bands of absorption in the spectrum of a solution of a salt of triphenylrosaniline. Both substances have a blue colour, differing only in intensity. The colour and the cause thereof are in each case the same.*

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