

THE SPECTROSCOPE IN ORGANIC CHEMISTRY.<sup>1</sup>

SOMEWHAT more than half a century ago, while engaged, with the assistance of Faraday, in preparing experiments for a Friday evening discourse in this institution, Stokes observed that the spectrum of the electric light extended to five or six times the length of the visible spectrum when he employed prisms and lenses of quartz instead of glass. This extension occurs at the violet end of the spectrum, and consists of rays of high refrangibility, to which the eye is insensitive, but which can be made apparent by means of a fluorescent screen.

At the time of this discovery, and in the years immediately following it, attention was being directed to the absorption of light by coloured solutions, and to the possibility of identifying coloured substances by the number and position of the dark bands in the spectrum of light transmitted through their solutions. Stokes saw that by his discovery of the extension of the spectrum beyond the visible region, this method of investigation might be applied to colourless as well as to coloured substances. In a paper communicated to the Royal Society in 1862, he says:—"Having

which we now possess of the relation between the structure of organic substances and the action of such substances on the ultra-violet rays, but the elaboration of the convenient and elegant methods by which such investigations are now conducted.

The light derived from an ordinary source of illumination, such as an electric lamp, consists of waves of all degrees of refrangibility, and its spectrum shows a continuous band of colour ranging from red to violet. The limits of this visible spectrum lie between the wave-lengths 7600 and 3900.

If now, instead of the electric light or other ordinary source of illumination, we employ the light emitted by one of the metals when raised to a high temperature, the spectrum is seen to consist of a series of lines of different colours and intensities lying within the same limits as the visible spectrum. But there are rays beyond the red end of the spectrum and rays beyond the violet end which excite no sensation of luminosity in the eye. By allowing the spectrum to fall upon a screen which has been coated with a fluorescent substance, such as sulphate of quinine or a salt of uranium, these rays are rendered visible for a short distance beyond the violet. But it is only when we replace the glass apparatus, with

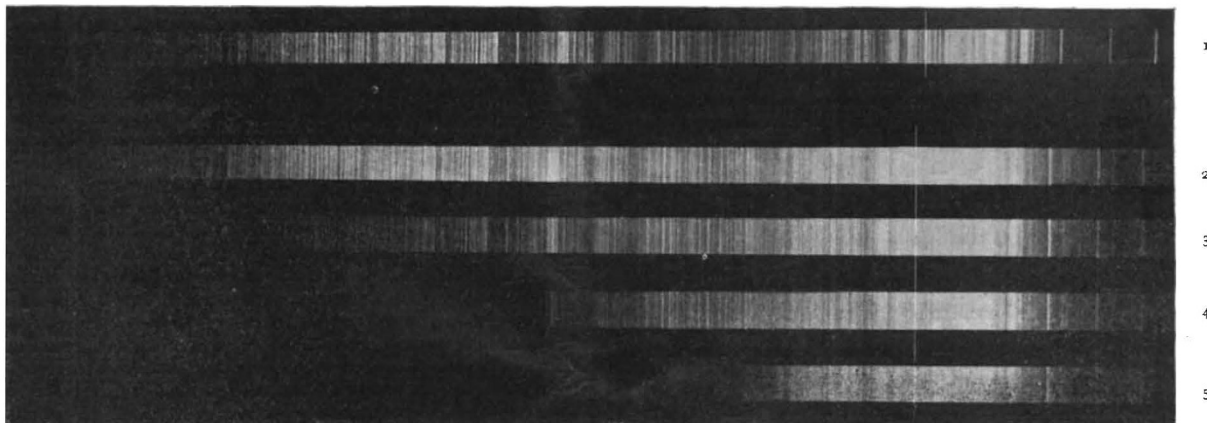


FIG. 1.—1. Spark spectrum of nickel and iron. 2. The same, after the light has passed through quartz 10 mm. thick. 3. Crown glass 0·13 mm. thick. 4. Crown glass 0·33 mm. thick. 5. Window glass 1·62 mm. thick.

obtained the long spectrum above-mentioned I could not fail to be interested in the manner in which substances—especially pure, but otherwise imperfectly known organic substances—might behave as to their absorption of the rays of high refrangibility." He proceeded, therefore, to study the action of various organic solutions on the ultra-violet rays, and found that the mode of absorption generally was so constant and so characteristic that by this single property many substances could be identified.

While Stokes was engaged in these researches, Prof. William Allen Miller was simultaneously at work in the same field, and Stokes left the further development of the subject in his hands. Miller improved the method of observation by substituting a photographic plate for the fluorescent screen, but he failed to "trace any special connection between the chemical complexity of a substance and its diastinic power." Struck by this fact, W. N. Hartley—now Sir Walter Hartley—commenced a systematic investigation of the whole subject, and it is to his researches, extending over a period of more than thirty years, that we owe, not only most of the knowledge

which we have hitherto been working, by a quartz prism and lenses, and substitute a photographic plate for the eye, that the full extent of the spectrum beyond the violet is revealed. This is the ultra-violet region—the region which Stokes opened up to investigation, and it is with the behaviour of organic substances towards the rays of this part of the spectrum that we have mainly to do this evening.

When light is transmitted through a coloured solution certain rays are absorbed, and dark bands corresponding to these rays appear in the spectrum. The importance of these bands as a means of distinguishing coloured substances has long been recognised, and, as we have already seen, considerable progress had been made with their study fifty years ago. As the bands in this case are in the visible spectrum, no special means are required for their observation.

But when we extend this method of investigation to colourless substances we are dealing with phenomena which lie hidden from the unaided eye, and our investigations are necessarily carried out with the help of photography.

The instrument employed in the study of absorption spectra consists of a spectroscope in which the eyepiece of the telescope is replaced by a camera. The

<sup>1</sup> From a discourse delivered at the Royal Institution on Friday, April 4, by Dr. J. J. Dobbie, F.R.S.

photographic plate is set at such an angle as to bring all the rays emanating from the source of light into focus at its surface after they have passed through the resolving prism, and for this purpose it is necessary that the plate should have a very slight curvature. The prisms and lenses of the apparatus are made of quartz, which, unlike glass, is readily permeable by the ultra-violet rays (Fig. 1). The source of light usually employed is that obtained by sparking one of the metals, such as iron, or a combination of metals, such as cadmium alloyed with lead and tin. In using the apparatus a photograph is first taken of the spectrum of the source of light. A layer of the substance to be examined, which, if a solid, must be dissolved in a suitable diactinic solvent, such as alcohol or water, is then interposed between the source of light and the slit of the collimator, and

the absorption bands, but their degree of persistence, *i.e.* the range of concentration within which they are exhibited. It is necessary, therefore, to vary the concentration of the solution or the thickness of the layer so as to cover the whole phenomena of absorption. This is done by simply diluting the solution, or diminishing the thickness of layer, on one hand, until the entire spectrum is transmitted, and on the other by increasing the concentration or the thickness of the layer until no further characteristic absorptive effect is produced. Photographs are taken at each concentration, and a curve is drawn connecting the concentration and the absorption as measured with reference to the lines of the metal employed as a source of light (Fig. 3).

If we now inquire whether the substances which affect light in one or other of the different ways

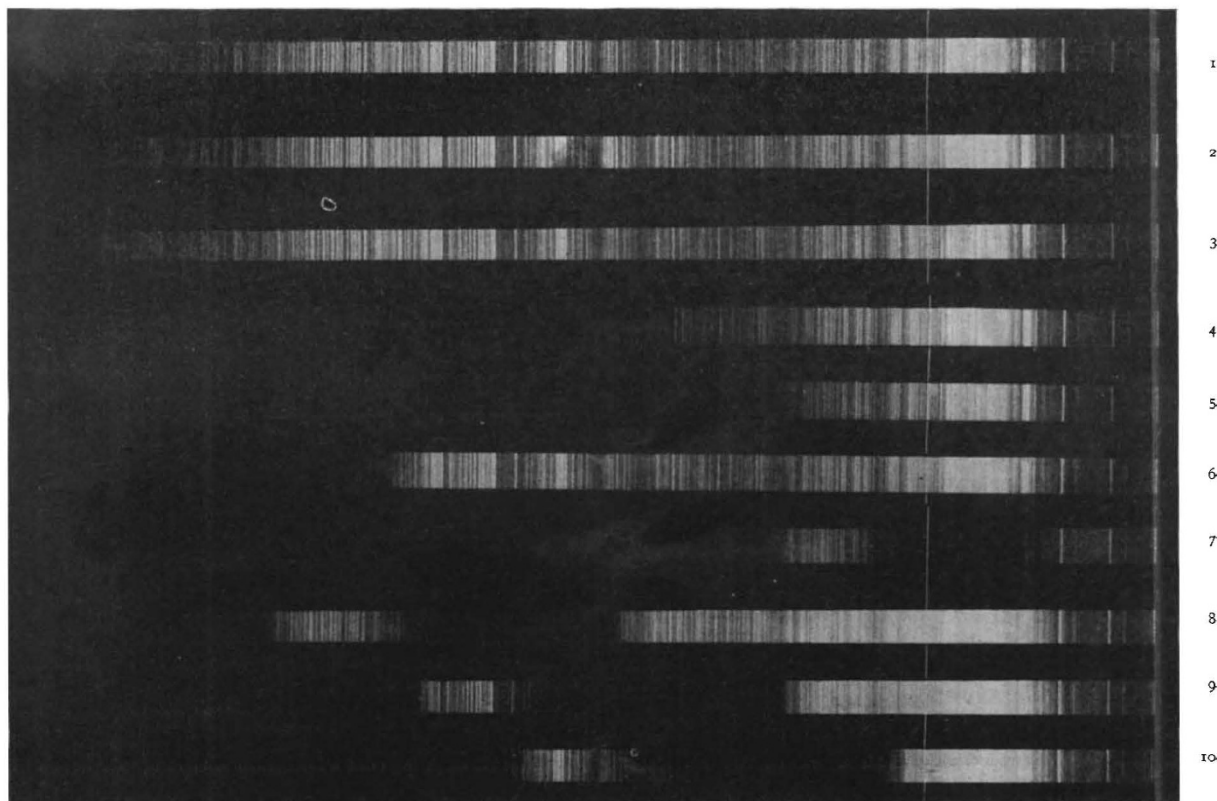


FIG. 2.—1. Spark spectrum of nickel and iron. 2 and 3. The same after the light has passed through water and solution of cane sugar respectively. Alcoholic solutions of (4) pinene, (5) thiophen, (6) citric acid illustrate general absorption, and alcoholic solutions of (7) isatin, (8) phenol (9) salicylic acid, (10) quinine hydrochloride illustrate selective absorption.

another photograph is taken. By comparison of the two photographs it is seen what effect, if any, the substance has had upon the transmission of the light.

When organic substances are examined in this way it is found that some allow light to pass freely through them. Others shorten the spectrum by absorbing the rays at the ultra-violet end to a greater or less extent, and are said to show general absorption. Others, again, possess the remarkable property of absorbing rays of a particular wave-length, thereby producing gaps or bands in the spectrum; these are said to show selective absorption (Fig. 2).

In studying these phenomena in their relation to the chemical characters of a substance, it is of importance to determine not only the extent of the general absorption and the number and position of

already indicated have themselves anything in common, we find that it is with those which possess the structure characteristic of benzene and its derivatives that the power of absorbing the rays of particular parts of the spectrum is most frequently, although not exclusively, associated.

Organic compounds, or compounds containing the element carbon, are divided into fatty or aliphatic, in which the carbon atoms are united in an open chain, and cyclic, in which the carbon atoms form a closed chain or ring. Hexane, which is a constituent of liquid paraffin, may be taken as an example of the first class. This substance possesses the formula  $C_6H_{14}$ . It is highly diactinic or transparent to the ultra-violet rays, and nearly all compounds belonging to the same division of organic chemistry, such as alcohols sugars,

and fatty acids, are either equally transparent to light, or only cut off a portion of the extreme ultra-violet rays of the spectrum.

If we now remove one atom of hydrogen from each of the two end carbon atoms of hexane, these atoms are in a condition to unite directly with each other, thus closing the chain. The substance so formed belongs to the cyclic division of organic compounds. It is known as cyclohexane, and has the formula  $C_6H_{12}$ , each carbon atom having two hydrogen atoms attached to it. This substance resembles hexane generally in its chemical properties, and behaves towards light in the same way, that is to say, it is practically diactinic or only cuts off some of the rays of light at the extreme ultra-violet end of the spectrum.

But a wholly different condition is brought about if we suppose one atom of hydrogen removed from each of the six carbon atoms of cyclohexane. One linkage is thus set free in each of the six carbon atoms, and we obtain benzene. How these linkages

group hydroxyl, we get substances belonging to the class of alcohols, and these substances are, like their parent substances, highly diactinic. If, on the other hand, we replace an atom of hydrogen in benzene by the same group we get carbolic acid or phenol, which, like benzene, exercises selective absorption on the ultra-violet rays, but gives a spectrum widely different from that of benzene.

Having dealt with the most general relation that has been observed between the structure of organic substances and their action on the ultra-violet rays, I propose to illustrate some of the more special relations by examples from the phenomena of isomerism. By replacing an atom of hydrogen in carbolic acid or phenol by the nitro-group we obtain three distinct nitrophenols. The ultimate particles or molecules of these nitrophenols are all composed of the same elements—carbon, hydrogen, oxygen, and nitrogen—and of the same number of atoms of each element. Such substances are said to be isomeric, *i.e.* they are made up of equal parts, although they do not possess

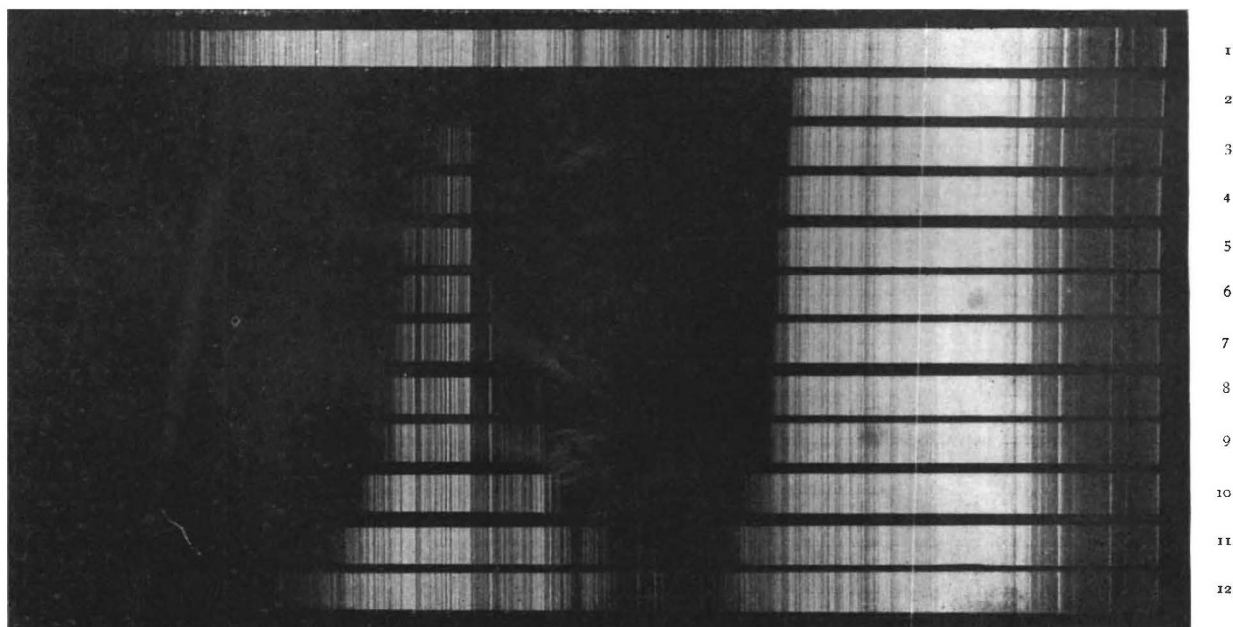


FIG. 3.—1. Spark spectrum of nickel and iron. 2 to 12. The same after light has passed through layers of 0.001 normal solution of salicylic acid from 90 to 4 mm. thick.

are actually employed in benzene has never been determined with certainty. Sometimes they are represented as mutually neutralising one another, sometimes as effecting a double link between the alternate pairs of carbon atoms. However this may be, the structure which bears the relation that I have indicated to the structure of hexane and cyclohexane is characteristic of the large group of organic substances of which benzene is the type. It is to this division of the cyclic compounds that the great majority of substances which show selective absorption, *i.e.* produce breaks or dark bands in the spectrum, belong. Here, then, we have a very important and a very general relation between the structure of organic substances and their absorption spectra.

The difference in the behaviour of organic bodies towards the ultra-violet rays, as exemplified in hexane and cyclohexane, on one hand, and benzene on the other, is brought out very clearly when we examine some of their derivatives. If we replace an atom of hydrogen in hexane or cyclohexane by the monovalent

the same properties. The difference between them lies in the arrangement of the parts relatively to each other; in this case in the position of the nitro-group in relation to the hydroxyl group. On comparing the spectra of the three nitrophenols we find that they differ in quite a marked manner from one another, and afford an illustration of the important general rule that substances which have the same composition but different spectra differ in structure.

It will have been noticed that the substitution of the nitro-group for hydrogen in phenol has the effect of shifting the absorption band nearer to the visible region. One of the three nitrophenols has a yellow colour, and in this case the gap in the spectrum cuts a little way into the violet end of the visible region. By the addition of soda to the solution the colour is changed to red, and on examining the spectrum of this solution we see that the gap now extends far into the visible region. This example will serve to illustrate the close connection that exists between the

study of absorption spectra and the origin of colour, an interesting branch of the subject with which, however, it is impossible for me to deal within the limits of this discourse.

In the nitrophenols we have an example of what is known as structural isomerism, or position isomerism, because the phenomenon depends upon differences in the position or arrangement of the atoms within the molecule—in other words, in the internal structure of the molecule. But it is possible to have two substances of the same composition and structure not identical, but related to one another as an object is to its mirror-image. Substances so related are termed optical-isomers or stereo-isomers. The spectra of isomers of this class, unlike those of structural isomers, do not differ. This leads to an important application of absorption spectra in chemical investigations. If two substances have the same composition but different spectra, we know that they must be structurally different; if, on the other hand, they have the same composition and the same spectra,

The structure of methyl-isatin and of methyl-pseudo-isatin has been determined by chemical methods, but the structure of the parent substance isatin cannot be determined in this way. Is it constituted like methyl-isatin or like methyl-pseudo-isatin? Inspection of the photographs of the spectra of the three substances shows that while there is a wide difference between the spectra of isatin and methyl-isatin, the spectra of isatin and methyl-pseudo-isatin are almost identical, as we should expect them to be on the view that they are constructed alike.

This phenomenon, which is known as tautomerism, is due to the fact that some substances contain an atom of hydrogen, or it may be a hydroxyl group, which readily shifts its position within the molecule, leaving its union with one atom to attach itself to another. Another example of this is afforded by cotarnine, a substance found in opium. The molecule of cotarnine possesses an atom of carbon which is directly combined with an atom of nitrogen, and has also united to it a hydroxyl group. Under the influ-

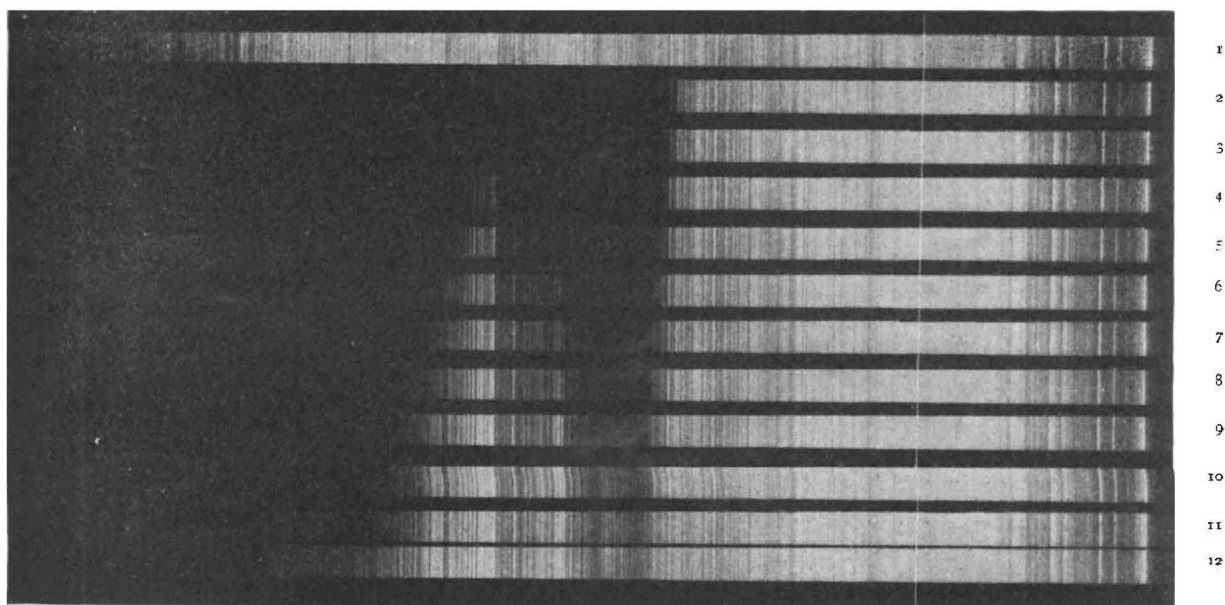


FIG. 4.—1. Spark spectrum of nickel and iron. 2 to 12. The same after the light has passed through layers from 60 to 4 mm. thick of an alcoholic solution of morphine containing  $\frac{1}{100}$  grain of the alkaloid.

and yet are not identical, there is a strong probability although not a certainty, that they are optical-isomers.

The study of absorption spectra has proved of special value in the investigation of substances capable of existing in two forms which may pass the one into the other. It is rarely the case that both forms of such substances are stable, and it is often extremely difficult, or altogether impossible, on account of this instability, to determine by the ordinary chemical processes which of the two possible forms the substance as we know it possesses. Such substances, however, frequently give rise to two series of stable isomeric methyl- or ethyl-derivatives, the structure of which can be ascertained by chemical investigation. The parent substance, if not a mixture of the two forms, must correspond in structure with one or other of these derivatives, because it is a well-established fact that the introduction of the methyl- or ethyl-group into a substance in place of an atom of hydrogen does not appreciably alter the spectrum.

An example of this is afforded by the three substances isatin, methyl-isatin, and methyl-pseudo-isatin.

ence of certain reagents the hydroxyl group leaves the carbon atom and attaches itself to the nitrogen atom, but can readily, by an alteration of the conditions, be enticed back again to the carbon atom. The shifting of the position of the hydroxyl group is accompanied by other changes which, however, it is not necessary that we should take into account for our present purpose. In this case both the tautomeric forms are, under certain conditions, stable. The form in which the hydroxyl is attached to the carbon is colourless, while the form in which it is attached to the nitrogen is yellow. The two forms have totally distinct absorption spectra. When one of the forms passes into the other under the influence of the appropriate reagent, the amount of change is proportional to the quantity of reagent added. It is possible, therefore, by taking photographs after the addition of each successive quantity of reagent, to trace the progress of the change through all its phases, and to ascertain how much of each form is present at any time. This is done by comparison with a series of reference plates prepared by photographing mixtures

in various definite proportions of two derivatives of cotarnine which possess the same spectra as the two parent forms.

The study of the absorption spectra of the alkaloids has been applied with success, not only to the investigation of their structure but to their detection and estimation. These substances generally have very characteristic spectra by means of which they can be distinguished with certainty from one another, except when they are homologous or otherwise very closely related structurally. The spectroscopic method may, therefore, be used with great advantage in examinations for the presence of alkaloids to confirm the results obtained by the usual chemical tests. The chemical tests are no doubt as a rule sufficiently distinctive, but considering the gravity of the circumstances in which they have frequently to be applied, it is unnecessary to insist on the value of the confirmatory evidence which can be obtained by the use of the spectroscope.

The minutest quantities of alkaloids can be detected by this means, the method rivalling the colour reactions for the alkaloids in delicacy. Thus, with a quantity of strychnine not exceeding 1/500 of a grain, a clearly defined spectrum of the alkaloid can be obtained. The photograph of morphine already shown was obtained with 1/200 of a grain of the alkaloid, and that of nicotine with 1/100 (Fig. 4).

The use of the spectroscope in the detection and estimation of alkaloids in cases of poisoning possesses certain advantages of the highest importance. One is that the material is not destroyed. The solution which has been employed for the spectroscopic examination can be used afterwards for the chemical examination. Another is that a permanent record is obtained which is always available for reference.

So far my illustrations have been confined almost entirely to colourless substances, because it is in connection with the investigation of such substances that most of the recent advances in the subject have been made.

As my last example, I shall take the case of a coloured substance in which the method has been applied within the last year with marked success.

It will be remembered that considerable uneasiness was caused when it became known some time ago that nitrogen peroxide is sometimes employed to bleach flour. In the course of an inquiry into the subject, it became necessary to determine the nature of the colouring matter naturally present in flour. It was known that many of the yellow and orange pigments so widely distributed throughout the vegetable kingdom are either closely connected or identical with carotene, the orange colouring matter of carrots, and it had been suggested that the colouring matter of unbleached flour might be identical with, or belong to the same class of colouring matters as, this substance. It was impossible, however, to prove this by the usual chemical methods, because the amount of colouring matter in flour is so minute that its isolation in a pure state, and in sufficient quantity for chemical analysis, was scarcely practicable. Carotene, however, can be prepared in a pure state, and the happy idea occurred to Dr. Monier Williams, of the Local Government Board, who was conducting the investigation, to photograph its absorption spectrum and compare it with that of the colouring matter of flour, which could easily be obtained in the minute quantity required for this purpose. Inspection of the photographs shows that the spectra are very similar. There cannot, therefore, be any doubt that the colouring matter of flour, if not identical with, is closely allied to, carotene.

The underlying causes of the relations between

chemical structure and absorption spectra have been the subject of much speculation, but it must be confessed that no satisfactory explanation of the phenomena of absorption has yet been formulated, and that the theoretical development of the subject lags behind its practical application.

#### UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

ON the occasion of the installation of the Duke of Northumberland as Chancellor of Durham University on May 3, honorary degrees of the University were conferred on the following men of science:—*D.C.L.*, Lord Rayleigh; *D.Sc.*, Sir Archibald Geikie, *K.C.B.*, *P.R.S.*, Sir William Ramsay, *K.C.B.*, Sir T. C. Allbutt, *K.C.B.*, Sir J. A. Ewing, *K.C.B.*, Sir William Crookes, *O.M.*; Sir J. J. Thomson, *O.M.*, and Prof. E. B. Poulton.

IN the House of Commons on Monday, May 5, Mr. Asquith, replying to several questions referring to the recent decision of the Convocation of the University of Oxford as to Divinity degrees, said:—"I have for a long time had under consideration the various proposals for the appointment of a Royal Commission or Commissions to inquire into the constitution of, and other matters connected with, the Universities of Oxford and Cambridge. I have reluctantly come to the conclusion that in existing circumstances the setting up of such an inquiry might lead to delay in the prosecution of necessary reforms and is not likely to be productive of fruitful consequences."

THE first session of the new University of Western Australia was inaugurated on Monday, March 31, with an address on the place of mathematics and physics in a university education, by Prof. A. D. Ross. About 150 students have enrolled in the faculties of arts, science, engineering, and agriculture. At present the teaching is being carried on under considerable difficulties, as the portion of the temporary buildings which has already been erected does not afford accommodation for laboratory instruction. The work of extending the premises is, however, being pushed on rapidly, and the various science departments should be in a position to carry on their practical work in the third term.

THE April number of *The Eugenics Review* is mainly occupied with the report of the Eugenics Education Conference, which took place on March 1, and was reported in *NATURE* of March 6. As a practical outcome of the conference a deputation, having for its object the introduction of teaching of eugenics in training colleges, waited on Mr. Trevelyan, *M.P.*, at the offices of the Board of Education on April 2. The deputation, which included, among others, the president of the Eugenics Education Society, the Dean of St. Paul's, the headmaster of Eton, the principal of Bedford College, and Mr. Nicholls, ex-president of the National Union of Teachers, was sympathetically received by Mr. Trevelyan, who said that the Board of Education recognised the importance of the matter referred to, and would consider carefully the recommendations made by the deputation. From the "Notes" column of the review we learn of the formation on January 29 of the *Société Française d'Eugénique*. The president of this society is M. Edmond Perrier, the general secretary M. le Dr. Apert, and the treasurer and librarian M. Lucien March. In Italy a eugenics society is in course of formation, and in Denmark, at the instigation of Dr. Soren Hansen, a eugenics section of the Anthropological Committee has been organised. The research committee of the Eugenics Education Society