time the results were uniformly unsatisfactory. Finally, in 1815, the secret was accidentally discovered. Tests had been made in a rolling mill at Schuylkill. After repeated attempts to make it burn by means of frequently raking the fire, the workmen gave up the experiment in disgust, filled the furnace with the worthless "black stones" and left it. Returning a few hours afterward, they were amazed to find a fierce fire with a terrific heat, and thenceforward the problem of burning anthracite was solved.

But the people were slow to believe that it was possible to get heat by burning the black stones. As late as 1833 one Charles Miner wrote as follows: "While we pushed forward our labors at the mine, hauling coal, building arks, etc., we had the greater difficulty to overcome of inducing the public to use our coal when brought to their doors, much as it was needed. We published hand bills in English and German, stating the mode of burning the coal, either in grates, smiths' fires or in stoves. Numerous certificates were obtained and printed from blacksmiths and others who had successfully used the anthracite. Mr. Cist formed a model of a coal stove and got a number cast. Together we went to the several houses in the city and prevailed on the masters to allow us to kindle fires of anthracite in their grates, erected to burn Liverpool coal. We attended at blacksmiths' shops and persuaded some to alter the 'too-iron,' so that they might burn the Lehigh coal; and we were sometimes obliged to bribe the journeymen to try the experiment fairly, so averse were they to learning the use of a new sort of fuel so different from what they were accustomed to."

But even these methods were slow to overcome popular prejudice. It was only when, through a sudden rise in the price of charcoal, the manufacturers began to use anthracite that the new fuel found its way into favor.—Toronto Post and Express.

RECENT DEVELOPMENTS IN COLORING MATTERS.*

GEHEIMRATH PROFESSOR OTTO N. WITT, Ph.D., F.C.S., of Berlin.

THE love of color is innate in the human mind, and this alone, if nothing else, would be sufficient to account for the interest with which the coal-tar color industry has met from its beginning. In England especially its progress has been watched with great attention, and only two days ago the Vice-Patron of this institution, His Royal Highness the Prince of Wales, has shown by some remarks, made in his opening address of the New Technical Institute at Bushey, that the interest taken in this subject has in no way abated.

Artificial coloring matters have formed so often the subject of more or less popular lectures, and this subject has been treated with such ability by eminent scientists, that it becomes difficult to show this domain of chemistry in a light new and interesting to an audience such as I have to-day the honor to address. Many years ago you have seen in this room the early achievements of the newly-created industry, marvelous for their beauty and brilliancy. Later on the progress of this industry has been duly recorded. More recently still it has become the custom in this country to view color making not so much from its chemical or industrial side, as from the standpoint of the national economist, who contemplates the values produced by industrial enterprise, and investigates the reasons why these values should be unevenly distributed among the different nations, striving side by side for progress and engaged in friendly, yet none the less eager, competition.

I may say at once, that I have no intention to treat my subject from either of these points of view. I take it for granted, that everybody is acquainted with the marvelous variety and brilliancy of artificial dye-stuffs, and I am too much of a chemist and too little of an economist to offer any original or valuable view about that side of the question which I have just mentioned. But I shall make an attempt to trace in this lecture the influence of the development of theoretical chemistry on the progress of the color industry. If in so doing, I should refer now and then to theoretical points without being able to explain them in detail, I hope to be forgiven.

In beginning this lecture allow me briefly to refer to the history of it.

When I received from Sir William Crookes the flattering invitation to speak before you this evening, my thoughts naturally wandered back to some recollections in connection with this institution. I remembered vividly several brilliant lectures to which I had the privilege of listening in this room, where the spirits of Davy and Faraday, of Graham and Huxley, of Würtz and of my immortal friend A. W. von Hofmann seem still to be hovering. I felt loth to raise my own voice in such hallowed precincts. But then I also remembered an almost forgotten episode in my own life, which I ask your permission to tell.

I remembered that almost exactly five-and-twenty years before receiving this invitation, I, then a very young chemist, had read before the Chemical Society of London, a paper containing a then somewhat daring speculation on the connection of the constitution of coloring matters with their properties, a paper which the publication committee refused to print. A lively discussion followed, which was wound up by some encouraging remarks from the president, the late Mr. De la Rue. He said that he hoped that this speculative paper would prove useful in clearing up the complicated domain of coloring matters and that perhaps on some future occasion I should be in a position to place before the world, in a Royal Institution lecture, the results which had been obtained by its help.

This strange reminiscence, coupled with the curious fact that Mr. De la Rue's prophetic words were fulfilled just when the period commonly assigned to a jubilee had elapsed, gave me the courage to accept Sir William's kind invitation. For though I have done comparatively little toward the increase of our knowledge of coloring matters, the five-and-twenty years past have sufficed to shed a brilliant light on what Mr. De la Rue could then justly call a very imperfectly known domain of chemistry, and innumerable facts brought to light during this period by a whole army of assiduous workers are now by common assent being classified under a theory which is neither more nor less than the suggestions contained in that rejected paper of mine, which I had fortunately published in another journal.

I may add that I have been guilty in later times of another theory, which refers to the domain of dyeing, and which has still many opponents. This theory is the direct outcome of the theory of coloring matters, and may be illustrated by some simple, yet striking experiments, some of which I intend to show you.

A fundamental question in the chemistry of dye-stuffs, and one not at all easy to answer, is this: "What is a dye-stuff?" Clearly it is something totally different from a substance only endowed with the power of selective absorption of light, a power which causes it to appear colored. We know now that there are more substances in creation which possess this power than bodies which lack it. In this very room we have learned that the air itself, through which the solar rays penetrate on to the surface of the earth, is blue, and not colorless, as we used to think. But even if we leave out of the question such faintly colored substances as air and water, if we restrict our consideration to compounds endowed with a very intense power of selective absorption and at the same time soluble in the water which we employ for preparing our dye-baths, we do not arrive yet at the true definition of the dye-stuff. Cupric salts, soluble chromates and many other intensely-colored bodies are no dye-stuffs, as may be easily shown by experiment. Yet these compounds penetrate into the interior of textile fibers which are immersed into their solution. They must do so, according to the laws of Osmose so ably expounded by Thomas Graham, because they are crystalloids and the fibers are invariably colloids.

We know now that the laws of Osmose are identical with the laws governing solution, and that crystalloids are able to wander into the interior of colloids because they are soluble in their substance. Osmotic processes may be observed between two liquids which cannot be mixed with each other, just as well as between a liquid and a colloid immersed into it. Consequently we are justified in assuming that the same powers are at work in both cases.

In my first experiment (Exp. I.)* I intend to show you that a crystalloid, dissolved in some liquid such as water, and brought into contact with another liquid, not miscible with the first, such as ether, will remain indifferent to the ether altogether, or it will leave the water and wander into the ether, or it will be distributed according to a certain ratio between the two solvents. In this latter case we have reason to believe that a constant interchange of molecules takes place between the two solutions. Clearly, this will only happen if there exists no great difference in the solubilities of the crystalloid in water and in ether. In that case the water will continually abstract nearly as many molecules of the crystalloid from the ether as the latter will take up from the water, and thus an equilibrium will be reached. If, on the other side, there is a great dissimilarity in the solubility of the crystalloid in the two solvents, then this process of mutual interchange will become so one-sided that it practically amounts to the absorption of the whole of the crystalloid by one of the solvents.

My second experiment (Exp. II.)† is a more striking illustration of these fundamental facts. If we mix together two colored solutions, one an aqueous one of a substance much more soluble in ether than in water, and the other an ethereal one of a substance more soluble in water than in ether, then the two solutions, on shaking, change color, and their shades are reversed.

According to my theory, the process of dyeing, considered so problematical by many experts in this ancient and useful art, is strictly analogous with this wandering of molecules governed by the laws of solution, which we can so easily observe and control in operating with two non-miscible liquid solvents.

In my next experiment (Exp. III.)‡ we see that a dye stuff wanders from the bath on to the fiber in much the same way as it wandered from water into ether. And if the fiber be previously dyed with a coloring matter little soluble in its substance, then this may be expelled and replaced by another of greater solubility. (Exp. IV.)

We see now that, in order to become a dye stuff, a substance must not only be so intensely colored that it can communicate its own shade to colorless substances holding it in solution; it must not only be soluble in water or any other liquid suitable for preparing a dye bath; but it must also be soluble, and even much more soluble than in water, in the colloid, which forms the substance of the textile fiber. The finished dyed fabric is nothing more nor less than a solid solution of the dye stuff in the substance of the fiber, unless there are secondary chemical influences, such as that of the mordants, at work, which change the solution into a suspension by precipitating the dye stuff after its immigration into the fiber.

This peculiar combination of solubilities is very rarely met with among the colored substances of an anorganic nature. In the vast domain of organic compounds of the aliphatic series we meet with very few dye stuffs, because its members are mostly colorless, or but very faintly colored. In the aromatic series, on the contrary, the power of selective absorption of light is so very frequent, that it would be very curious indeed if just that combination of solubilities, which is the making of the dye stuff, were not of common occurrence. Taking as a basis the universally admitted

* Details of experiment: An aqueous solution of magenta does not yield its coloring-matter to ether; indophenol, on the contrary, is entirely taken up by ether. The dye-stuff, which is partly taken up by ether, is also a member of the indophenol group, the constitution of which is not yet fully established.

† The ethereal solution used contained magenta acetate, while the aqueous one was prepared with trichloro-indophenol.

‡ In Exp. III. wool was dyed with erythrosine in the ordinary way, while in Exp. IV. a cotton cloth, previously dyed with patent blue, was treated in a bath of Congo red.

axiom, that the physical properties of every compound are direct functions of its molecular constitution, we may easily believe that that peculiar combination of solubilities which I have shown to be the characteristic feature of the dye stuff, would be the result of certain general conditions fulfilled in the constitution of many members of the aromatic group. My theory, proposed five-and-twenty years ago, was nothing else than an attempt to ascertain these general conditions by investigating the constitutional peculiarities of all those dye stuffs the constitution of which had been fully established in those days.

I have no intention to tax your patience by explaining in detail the results of that old investigation. It will be sufficient to summarize them by saying that in the molecule of every coloring matter, the constitution of which has been ascertained to this day (and there are many thousands of them), certain atomic constellations have been observed which seem to be essential, and of which always two must be present. One of these constellations is a group of atoms, which is the cause of the selective absorption of light. This group of atoms I called a *chromophore*. The number of atomic groups endowed with chromophoric properties amounts at present to about two dozen, and is being constantly increased by the progress of chemical research. All the chromophores, however, have that in common, that they are unable to exert their influence unless they are helped by the presence of another group of atoms, which I call the *auxochromic* group. Very few auxochromic groups are known, and they belong to those which occur most frequently in the whole domain of organic chemistry—the amino group in its various forms, the hydroxyl group occurring in all the phenols, the sulpho and the carboxyl group. None of these will cause a substance to become a dye stuff unless this substance also contain a chromophore, but the latter is equally helpless if deprived of the assistance of the auxochromic group. Thus we meet in the molecular world that condition of the necessity of mutual help and assistance between two heterogeneous forms, which we can also trace in sociology, a fact the establishment of which will no doubt be greeted with satisfaction by the ladies in this audience.

Our ideas on the nature and constitution of those groups which may act as chromophores have of course undergone many changes. Undoubtedly there must exist a law which governs the formation of chromophoric groups, but so far this law has not been definitely established. Some progress has, however, been made toward this end. At first the chromophores which we had gradually collected formed rather a motley crowd, and seemed to have no points in common. At present chemists working in this domain are inclined to attribute a quinoid structure to the great majority of coloring matters. If this view be correct, then all these substances would be derivatives, not of benzene and its congeners, but of hydrocarbons containing two hydrogen atoms more in their molecule, derived from dihydrobenzene as a prototype. As sometimes it is almost impossible to decide in favor of one view or the other, the convenient hypothesis of tautomerism was resorted to, but in some cases we have been able to establish definitely the quinoid formula. Such is the case with the large and brilliantly colored group of dye stuffs called phtaleines, which, according to modern view, must be considered as quinoid derivatives of benzoylbenzoic acid. The experiments which lead to this conclusion are so striking, that I cannot refrain from producing one of them, which has never been shown yet, though the time at my disposal does not allow its exhaustive discussion from a theoretical point of view. If we dissolve the well-known phenol-phtaleine in anhydrous ether containing some ammonia, the solution is perfectly colorless, but if we add ordinary water to this solution (Exp. V.), it assumes a beautiful red coloration. This peculiar fact that water alone is sufficient to cause the formation of this color is perfectly incomprehensible if the old views on the constitution of phtaleines, which are still given in the majority of text-books, be adhered to, but it is exactly what we might expect to happen if we assume that the ammonium salt of phenolphtaleine possesses a cycloid constitution in its ethereal solution, and that it is isomerized into the quinonoid form by the addition of water.

Thus our knowledge of the chemical causes of the physical properties of coloring matters is continuously developing. Quite lately we have even begun to form definite views about the connection of the chemical constitution of aromatic substances with that peculiar form of selective absorption of light which we call fluorescence, and which has formed, from the physical point of view, the subject of the masterly investigations of Sir Gabriel Stokes. The phenomenon of fluorescence is very frequently met with in dye stuffs, and in the raw materials used for their manufacture. It can be exhibited in a very striking way with the help of electricity, either by allowing an arrow of electric light to penetrate into the solution of a fluorescent substance or by working a Geissler tube of suitable shape submerged in such a solution (Exp. VI.). The fact that the fluorescence of many substances is chiefly caused by the ultra-violet light, I shall try to demonstrate by the following, somewhat delicate, experiment: I have here, submerged in a solution of eosine, a Geissler tube, the lower part of which is ground out of a piece of rock crystal, while the upper half is made of glass. When the electric current passes this tube the fluorescence round the quartz part of it is stronger than that in the neighborhood of the glass, because the latter absorbs a good deal of ultra-violet light, while the quartz is almost free from such absorption. (Exp. VII.)

An immense amount of patient work has been accomplished by many chemists in the hope of establishing definite views on the constitution of the azo-colors, that group of dye stuffs the introduction of which into the color industry was the direct consequence of our early efforts to cast off empiricism, and to conduct our search for new coloring matters according to definite scientific principles. Simple and transparent as the constitution of azo-colors appears to be if viewed superficially, yet it offers some problems of extraordinary difficulty, which have not been solved so far. But

* Paper read before the Royal Institution of Great Britain.

fortunately these difficulties have in no way interfered with the technical development of this family of dye stuffs, which has been for a whole quarter of a century one continued and unparalleled series of successes. The process for producing these dye stuffs is of the greatest simplicity. It consists in pouring together (Exp. VIII.) cold aqueous solutions or suspensions of diazo-compounds and phenols or amines. The dye-stuff is formed at once in a state of absolute purity, and with a yield absolutely theoretical; it need only be collected and dried to form a salable product. No wonder, then, that these dye stuffs gradually became the leading ones, and to a great extent superseded the old empirical products which were concocted in many complicated operations, with yields very far from satisfactory. As the number of diazo-compounds and of phenols and amines at our disposal is very large, the number of dye stuffs which may thus be prepared is quite extraordinary; it has been computed, according to the rules of permutation, 3,159,000 different individual dye stuffs have thus been proved to be at present easily accessible to our industry. Of these at least 25,000 form the subject of German patent specifications and of corresponding specifications in England, France, the United States and other countries. Over five hundred are regularly manufactured on the larger scale.

The prolific nature of the azo-color reaction explains the fact, that in this group we can choose, much better than in any other, substances possessing that ratio of solubilities in water and in the colloid substance of the various textile fibers, which we require. We can produce, quite at will, azo-dye stuffs which dye wool or silk or cotton, which dye slowly or quickly, which will stand soap or acid or alkali. This possibility of adjusting the chemical properties of dye stuffs with an almost mechanical precision has been the cause of one of the greatest successes of the color industry, the introduction of what is now known under the name of "substantive dye stuffs," an expression which means dye stuffs that will dye cotton and other vegetable fibers from a simple aqueous dye bath without the use of any mordant. The difference of the solvent power of cellulose and of water is for the vast majority of dye stuffs so small, that the process of dyeing vegetable fibers with these ordinary coloring matters can only be compared to that case of the joint action of ether and water on some substance soluble in both these solvents, where an almost equal division of this substance takes place between the two solvents. Such cases exist, as you saw in the first experiment. It is among the azo-dyes that we have found compounds which are so much more soluble in cellulose than in water, that they readily leave their aqueous solution and take up their abode in the fiber. And we have not only found these dye stuffs but also the law which governs this most valuable abnormal solubility: it appears in all azo-colors, which are prepared with diazo-compounds derived from symmetrical para-diamines. A novel and extremely fertile field for a systematic search for new dye stuffs was thus opened, a field which has occupied hundreds of busy workers for many years, many of whom carried home a rich reward.

But while this field bore its rich harvest, others were by no means neglected. The search for dye stuffs, which will dye cotton without a mordant, could not make us forget that just those coloring matters which imperatively demand the use of mordants are those which from time immemorial have been used in preference for the production of fast and lasting shades. The brilliant synthesis of alizarine by Graebe and Liebermann, which made the world ring with admiration early in the seventies, had given us ample proof that the old and to this day not wholly forgotten axiom, that there are two kinds of dyes, natural ones, which are fast, and artificial ones, which are fugitive, was a preconceived idea, totally devoid of any scientific foundation. The enormous financial success of the alizarine industry formed a tempting invitation to search for other dye stuffs, which, similar to alizarine, would be endowed with the power of forming almost indestructible lakes with mordants of a sesquioxydic nature. Here, too, like everywhere in science, we have marched for some time on the paths of empiricism, but here, too, logical deduction has come to our aid in disclosing the laws which govern the formation of lakes. In this case it is not (as in the substantive azo-dyes) the carbonic nucleus which determines the *physical* properties (viz., the ratio of solubility) of the dye stuff, but it is the peculiar position of the auxochromic groups contained in the molecule, which governs its chemical properties. We know now, that a dye stuff must contain, in order to be able to form lakes with sesquioxydic mordants, two hydroxyl groups in juxta-position. If this condition be fulfilled, the dye stuff will dye in the same way and with equal fastness as alizarine, even if it be no derivative of anthracene, like the early alizarine dyes; and if these two hydroxyl groups or a suitable equivalent for them be missing it will lack all power of dyeing mordants, even though derived from anthracene. With this law once established the synthesis of mordant dye stuffs became a very easy matter, and to-day there is hardly a group of coloring matters in which there are not some members possessed of this peculiarity and owing it to the same uniform cause. Still the group of the oxyke-tones, to which alizarine itself belongs, remains the true home of mordant dyes, but this group has grown to-day into a very numerous and varied one. Mordant dyes of every shade are to be found in it, and cotton is no longer the only fiber to which such dyes are applied. It is a fact worthy of notice that among the many dyes of this class which we now possess and the constitution of which is fully established there is not a small number, the molecule of which contains three, four, five or even six hydroxyl groups. Yet this increase of auxochromic groups does not influence in the least the behavior of these dyes to mordants, this is only governed by the two hydroxyl groups in ortho-position, and any other such group introduced into the molecule only changes the shade, not the characteristic chemical properties.

A greater variety still than by the achievements of modern synthetical work will come into this group of mordant dyes by the progress of the elucidation of the constitution of the natural dye stuffs occurring in roots, barks and woods. A good many of them are

still unsolved mysteries, but there can be no doubt that they owe, like alizarine, purpurine and the other madder dye stuffs, their property of dyeing metallic mordants to the presence of hydroxyl groups in ortho-position in their molecule.

A very large and varied group of coloring matters, which for a long time resisted all attempts at unraveling their constitution, are the Saffranines, Eurhodines, Oxazines, Thionines, Indulines and other allied groups. They are now completely understood, and have been recognized as the amino and oxy-derivatives of certain peculiar substances such as the azines and azonium bases, the molecule of which possesses a ring structure. Here no longer carbon atoms only form the closed chain, but nitrogen, oxygen and even sulphur atoms participate in its structure and bring about the peculiar properties of the compounds. When this fact was at first ascertained it seemed sufficient for the explanation of the behavior of such compounds as dyes. It was only somewhat later on that we recognized that in these classes of dye stuffs especially a quinonoid structure is essential.

The greatest and most brilliant success of the chemistry of dye stuffs is, however, the industrial synthesis of indigo. This offers so many points of general interest, that I am sure to meet with your approval if I refer to it in some detail.

The indigo problem is one of the oldest problems of chemistry. When Baeyer took it up more than thirty years ago he found the ground well prepared by others who had worked before him. But his is the merit of having completely elucidated the constitution of this extraordinary product of nature. He and others have also shown various methods for the synthesis or artificial production of indigo. In the laboratories artificial indigo has been known for the last twenty years.

But in this case the scientific synthesis of a natural product proved to be by no means identical with the industrial one. Industrial methods can only enter into competition with nature if they work more economically than nature does. In the case of indigo there seemed to be little hope for fulfilling this condition. The most enthusiastic admirers of the modern synthetical industry could not help seeing that all evidence in our hands went against the probability of the practical synthesis of indigo, and just those who understood most of these things could least of all close their eyes to that fact. It could not be denied that every possible synthesis of indigo, those known as well as those which might still be expected, had to start from some aromatic derivative of benzene, containing one carbonic and one nitrogenous side-chain in ortho-position. Of all the products at our disposal which fulfill that condition, ortho-nitrotoluene is the most easily accessible. Now, taking it for granted that indigo could be prepared regularly and with good yields from ortho-nitrotoluene, there still remained that difficulty, that all the toluene produced in the world, even if we suppose that all the other uses to which this hydrocarbon is put at present could be suppressed, would not suffice for the production of the world's consumption of indigo.

If, under such circumstances, the industry of artificial dye stuffs continued to work at the indigo problem, it did so more for the general interest attached to it, and with a view to securing some of the finer applications of indigo in printing, than in the hope of being able to compete with the natural product in the great consumption of vat dyeing. If, on the other hand, the indigo planters in the far East showed but small apprehension of the danger of which they were occasionally warned, we cannot blame them for it; they had, no doubt, taken the advice of competent people, and these had told them what was correct according to the knowledge of the time.

The final result has shown all the calculations of experts to be wrong, but in such a way that they, too, can surely not be blamed for the error they committed.

The process by which indigo is at present manufactured on a colossal scale by the Badische Anilin und Soda-Fabrik in Ludwigshafen on the Rhine, is based on Heumann's synthesis of this most important dye stuff, which consists in submitting phenylglycine to a fusion with caustic alkali. Phenylglycine is prepared by the action of monochloracetic acid upon aniline. The yield of indigo obtained is a poor one, but it can be very much improved if, instead of phenylglycine, we take its orthocarbonic acid. In this we have again the presence of a nitrogenous and a carbonic side-chain in ortho-position. To prepare this acid we should have to start, according to the ordinary rules, from toluene, transforming it by a succession of operations. Thus we come again to toluene as a starting point, and to the difficulty already explained.

There is, however, one somewhat abnormal process of preparing the same compound from phtalic acid. It consists in converting this into phtalimide, and treating the latter with sodium hypochlorite. By a somewhat complicated reaction, the nature of which need not be explained, one of the carboxyl groups of the phtalic acid is replaced by the amido group, anthranilic acid is formed, and this, if treated with monochloracetic acid, yields phenylglycine-carbonic acid, which has proved so important for the manufacture of indigo. Now phtalic acid is prepared by a powerful oxydation of naphthalene, and naphthalene again is that constituent of coal-tar which is present in by far the largest quantity.

It is true that the process for transforming naphthalene into phtalic acid, which was the only one known at the time when all these facts were first recognized, gave very bad yields, and was at the same time costly. The whole indigo problem stood thus reduced to the problem of transforming naphthalene cheaply and economically into phtalic acid. This has been accomplished by the Badische Anilin und Soda-Fabrik by heating naphthalene with fuming sulphuric acid in the presence of mercury salts. Torrents of sulphur dioxide escape, and the whole process can only be carried out properly if the means be given to convert this gas again into fuming sulphuric acid, which may be used again for treating fresh quantities of the hydrocarbon. The new sulphuric acid process of the Badische Anilin und Soda-Fabrik has thus been of paramount importance for the working out of the indigo problem.

Some of the older synthetical methods of producing

indigo are so easy and rapid that they can easily be shown as a lecture experiment. If, for instance, we add a caustic potash solution to a solution of ortho-nitrobenzoic aldehyde in acetone, indigo is formed at once and settles out in dark blue crystalline flakes (Exp. IX.). The synthesis now in practical use is a little more delicate in its execution, but there are certain modifications of it which are rapid enough to be shown in a lecture experiment (Exp. X.).

The action of the alkali on the phenylglycine-carbonic acid does not at once produce indigo; a colorless derivative of the dye, indoxylcarbonic acid, or rather its potash salt, is formed at first, but if we dissolve this in hot water and introduce a current of air, it is at once and with a quantitative yield transformed into indigo which settles out in the shape of a crystalline deposit of infinitely fine division. This is collected in filter presses and delivered into commerce in the shape of a paste or a powder.

The industrial synthesis of indigo is extremely interesting, because it is a triumph not wholly due to chemical science. Science has shown the way to success, but it was quite unable to clear away the difficulties arising from practical and economic considerations. Here the representatives of our great industry had to advance independently and on paths for which theoretical knowledge could not serve them as a guide. Unlimited praise and admiration are certainly due to them for the masterly way in which they grappled with colossal difficulties and for the courage with which they staked millions on the realization of one great idea.

At the same time we cannot help feeling some regret for the indigo planters in the far East, who, after enjoying more than a century of easy prosperity, see now that more serious times are in store for them. They see the day coming when the indigo plantations will disappear, in the same way in which the madder fields of Avignon have vanished. But we are consoled by the knowledge that, especially for India, the time has already come, which has been so vividly described by Sir William Crookes, in one of his addresses to the British Association, as the future in store, sooner or later, for all humanity, the time when bread begins to be scarce. It seems to me that any one who, by bringing about some great commercial revolution such as we have seen in the indigo trade, causes land in India to become free for the growing of rice and other cereals, renders a great service to large numbers of poor natives, and need therefore not be blamed for lessening to some extent the prosperity of a class of people who have had an unusually good opportunity of accumulating wealth in the past.

It is a strange fact, that with indigo the history of the fight of the madder root against artificial alizarine is almost literally repeated in spite of the great difference of original conditions in the two cases. Madder was a product containing at its best only 4 per cent of actual coloring matter; the rest was useless fiber and obnoxious impurities which greatly hampered the dyer in his work. Alizarine, entering into competition with this natural product, was, on the contrary, the coloring matter in a pure state, and therefore not only cheaper but also much easier in its application. Indigo, such as we received it from India and Java, is a manufactured article, the best qualities of which contain 59, 60, or even 70 per cent of pure dye stuff, besides impurities which have always been considered as perfectly harmless. Thus the artificial product did not seem to have much scope for improvement as far as the quality came into consideration. Here again we have committed a mistake. We know now that the impurities are not harmless, and that the blues dyed with artificial indigo are quite as superior in brightness and purity of shade to those obtained with natural indigo, as alizarine reds were to madder reds. This has, however, not always proved to be an advantage for the manufacturers of artificial indigo. The world does not ask for bright indigo shades, and a good many prejudices in that respect had to be overcome before artificial indigo was admitted as a legitimate substitute for the natural product in some of its most important applications. Yet a simple consideration will show that it is always easy to deteriorate the brilliancy of a dyed shade, whereas no art of the dyer will suffice to produce brilliant shades on textile fabrics with dye stuffs that carry their share of dirty admixtures within them.

In its application to the fiber, indigo is perhaps the most remarkable of all dye stuffs, for it is the principal representative of that extraordinary class of coloring matters which must be applied by the vat process. This process, which consists in first reducing the dye stuff into a leuco-compound before applying it to the fiber, on which the original coloring matter is formed again by the action of the oxygen of the air, seems to have nothing in common with the ordinary dyeing processes. If, however, we consider it more closely, we come to the conclusion that vat colors are a class of dye stuffs in which the functions of dyeing and of selective absorption of light are distributed on two different forms of the substance, one of which contains two atoms of hydrogen more in its molecule than the other.

This theory is supported to some extent by the fact that, what we are pleased to call leuco compounds, are in the majority of cases by no means colorless. Indigo white itself is not white but yellow in its alkaline solution which we call a vat. Other vat dyes have leuco compounds which are even more strongly colored. Thus the leuco compound of indanthrene, a beautiful new coloring matter, is blue like indanthrene itself; flavanthrene, a yellow dye stuff, which has not yet left the laboratory of its inventor, has a blue leuco compound. One may say that with all vat colors the real dye stuff is the leuco compound which is afterward, when once fixed on the fiber, transformed into a pigment by the oxidizing influence of the air.

In 1825 Faraday discovered, in this very house, benzene; the original specimen, prepared by his own hands, is before you. We look upon it reverently, like on a sacred relic bequeathed to us by a master mind. But what a development has sprung from this first attempt to unravel the mysteries of the aromatic series! Our science as well as our industry have been revolutionized by the investigation of the derivatives of benzene, and the world has been embellished by the

gay and brilliant dyes of which it is the mother-substance. The study of the chemistry of these dye stuffs has become a domain of science which, for variety and fascination, can hardly be surpassed by any other. The deeper we penetrate into it the more it proves an inexhaustible mine of the most subtle scientific thought, yet one which never loses touch with practical life; it is interesting alike to the philosophical mind that wishes to revel in the wonderful perfection and order of nature, and to the philanthropic spirit which rejoices in seeing many thousands of hands occupied and princely fortunes produced by the utilization of what was only a short time ago a refuse and an encumbrance. It teaches a lesson even to those who are not attached to science and apt to consider it as a kind of pastime for people who lack ability for practical life. For they cannot help seeing that, in this case, the most intricate science has led to something eminently practical, commensurate to a standard which, though unknown to the Bureau International des Poids et Mesures, is to some people the only reliable one, viz., the one of £ s. d.

I am afraid that the high praise which I feel justified in bestowing on what has been the favorite pursuit of my life is not fully substantiated by the contents of this lecture. The subject which I had to treat is so vast, that all I have been able to say is nothing but a sketch or a programme of what would require a long series of lectures if full justice were to be done to it. My one excuse for attempting to sketch, in the short space of one hour, so vast a subject, is the place in which I had the honor to speak. An audience that has been addressed more than once by the pioneers of the chemistry of dye stuffs, by Faraday, Hofmann, William Perkin, and others, could, from one of the Epigones, not have looked for more than a few notes and additions.

THE SIGRISTE PHOTOGRAPHIC APPARATUS.

The sensitiveness of gelatino-bromide of silver emulsions has necessitated the use of shutters that permit of leaving the objectives open for but a fraction of a second. The question has been studied in all its phases for the last fifteen years, and a conclusion has now been about reached, from a theoretical as well as a mechanical standpoint, as to what may be expected from shutters mounted near the objective or near the plate.

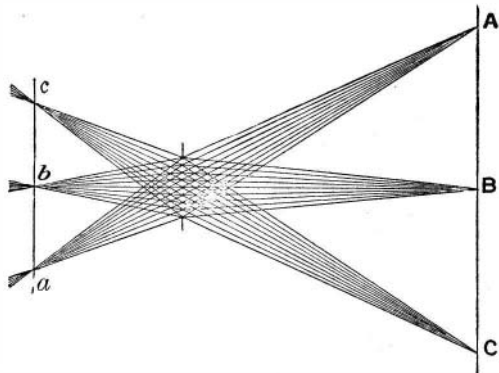When apparatus such as objectives, shutters, etc., are

FIG. 1.—COURSE OF RAYS IN A PHOTOGRAPHIC APPARATUS.

represented in elementary treatises upon photography, it is generally the custom to figure the course of the luminous rays that traverse them by two lines that intersect each other in the center of the objective. The result is that we readily imagine that the rays collectively form the two cones of which the apices touch one another in the center of the diaphragm. In reality such is not the case. From every point of the object ABC (Fig. 1) there emanates a pencil of rays that form a cone, and all these elementary cones having their apices situated at different points, have their common base at the diaphragm. As for the pencil that emerges

from the objective in the interior of the camera, that is formed of a similar system in opposite direction of which all the apices are at different points of the image ABC.

Upon considering this diagram we immediately see that a shutter mounted upon the objective cannot intersect all the pencils at once at a given point. There will always be a period of closing and a period of opening that will require an appreciable length of time. In practice these periods have finally been rendered very
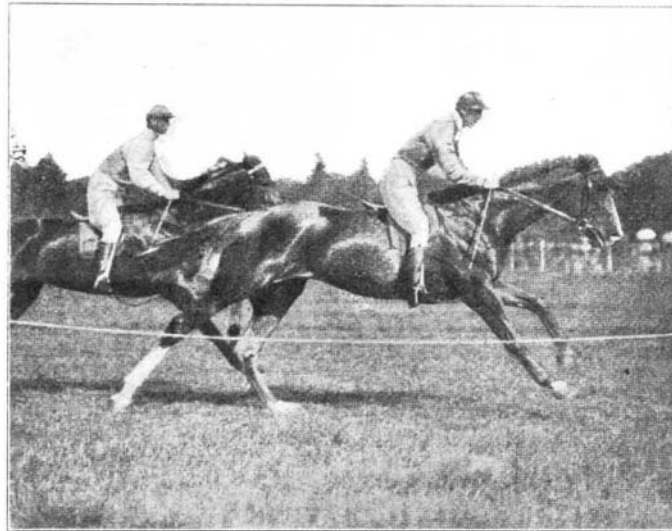
FIG. 3.—RACE HORSES PHOTOGRAPHED AT 5 METERS FROM THE APPARATUS.

short, and an interval of varying length left between them representing the time of effective exposure, that during which the objective is under the best conditions. Whatever may be done it is impossible to reduce these various periods beyond certain limits and that is why our most improved objective shutters cannot give us satisfaction for great speeds—when, for example, it is a question of obtaining a sharp image of an object passing sidewise and at a short distance. It is
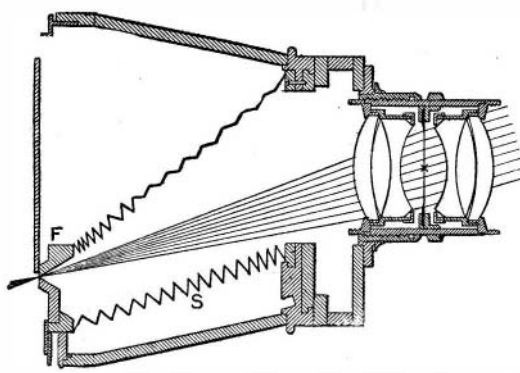
FIG. 2.—DIAGRAMMATIC SECTION, SHOWING THE MODE OF OPERATION OF THE SIGRISTE SHUTTER.

true that the case is rather rare, and that the shutters of the most widely used apparatus are sufficient for current practice. Our objection to them would rather be that they work too quickly, for it is better to operate in the shade than in the sun. But the ideal is certainly to have an instrument that permits of obtaining the two extremes, and such a result can be reached only with a shutter that passes over the plate. Such shutters generally consist of an opaque curtain provided with a slit that displaces itself along the plate. In this case all the light acts under the best conditions; but

it is easy to see (Fig. 1) that the efficiency will not be maximum unless the elementary cones are intersected at their apex. Provided that they present an appreciable extent at the place where the section is made, the obturation is no longer instantaneous, and this is a matter of great importance not only from the viewpoint of sharpness, but also in a general way, from that of the quality of the image.

Mr. Guido Sigriste, a painter of talent as well as a skillful mechanic and good mathematician, thoroughly realized the exigencies of shutters of this kind when he had recourse to photography for the study of horses running at high speeds After several years spent in tentatives and researches, he has succeeded in constructing an apparatus of maximum efficiency, which is a true instrument of precision. In fact, he has succeeded in making the slit through which the light passes, slide at 1-10 millimeter from the plate.

This slit, F, is formed of two strips of wood beveled at the edge and secured to the side carrying the objective through a skin bellows that follows it in its motions. (Fig. 2.)

The luminous pencils forming the image are, upon emerging from the objective, always comprised in this envelope; but their apices can reach the plate, through the slit, only successively, to the exclusion of any foreign light that might prove inimical to the formation of the image. This arrangement permits the light to act under the best conditions, even in the least favorable cases in which, as has been supposed here (Fig. 2), the objective admits very oblique pencils. As the edges of the slit have the beveled part turned toward the interior of the bellows, they arrest none of the elementary rays.

It is clear that this slit may be made more or less wide, at the will of the operator, who can vary it without opening the apparatus, and that its velocity can be regulated at will, as we shall show by a detailed examination.

The aspect is that of an ordinary twin camera (Fig. 4, Nos. 1 and 3). The finder consists of a frame M, an eyehole, H, and a sight, E, so arranged that the centering is always exact from a given distance. The shutter F (Fig. 2), is mounted upon a frame fixed to the extremity of the bellows, S, and sliding upon the back of the camera in such a way as to traverse the entire plate. The distance apart of the strips that form the slit may be varied by actuating a screw, V (No. 5), the square head of which engages in a cavity D that may be maneuvered from the exterior by means of a winch. A movable plate automatically closes the slit after the shutter has operated, so that the latter may be set anew without uncovering the sensitized plate. In order to change the plate and set the shutter, it suffices to actuate the magazine, P (No. 2), like an ordinary drawer. When pulled out it carries along a piece, F, to which is attached the extremities of a cord wound under the pulley seen at the lower part of the camera (No. 2), and that corresponds to the spring inclosed in the barrel, B (Nos. 5 and 6). When the drawer is at the end of its travel it is shoved back; but a tappet, T, retains the shutter, which remains in place.

Two buttons placed at the side of the apparatus, and capable of operating independently of one another, permit of disengaging the tappet, T. The slit then begins to move under the action of the spring, and, in order that it may keep up a uniform motion during its entire travel, two compensating springs, R, placed on each side offer an increasing resistance at the beginning, then straighten out, and finally aid in the motion. Experience has shown that perfect regularity is obtained in this way.

The velocity of displacement of the slit naturally depends upon the tension of the spring in the barrel, B, and this is determined by the maneuvering of a lever, L, (Nos. 4 and 6) that traverses the dial that may be seen in one of the sides of the apparatus (No. 5). The winch for the regulation of the slit is placed upon the side of the dial, and, at every revolution, causes the advance of an index that marks the width of the slit in half-millimeters.

The graduation that the operator has under his eyes is a function of the two important elements to be known, viz., the velocity of the displacement and the width of the slit. Both can be changed in an instant, and a glance at once shows under what condition the shutter is going to operate. To this intent it suffices to read the number inscribed upon the dial (No. 4) in the section occupied by the lever, L, and opposite the figure indicating upon the latter the width of the slit. The figures given here have been verified in a very precise manner by means of the D'Arsonval electric chronograph. The objective used may be of any make whatever. If it is desired to obtain photographs of race horses for which the time of exposure is 1-2800 of a sec-
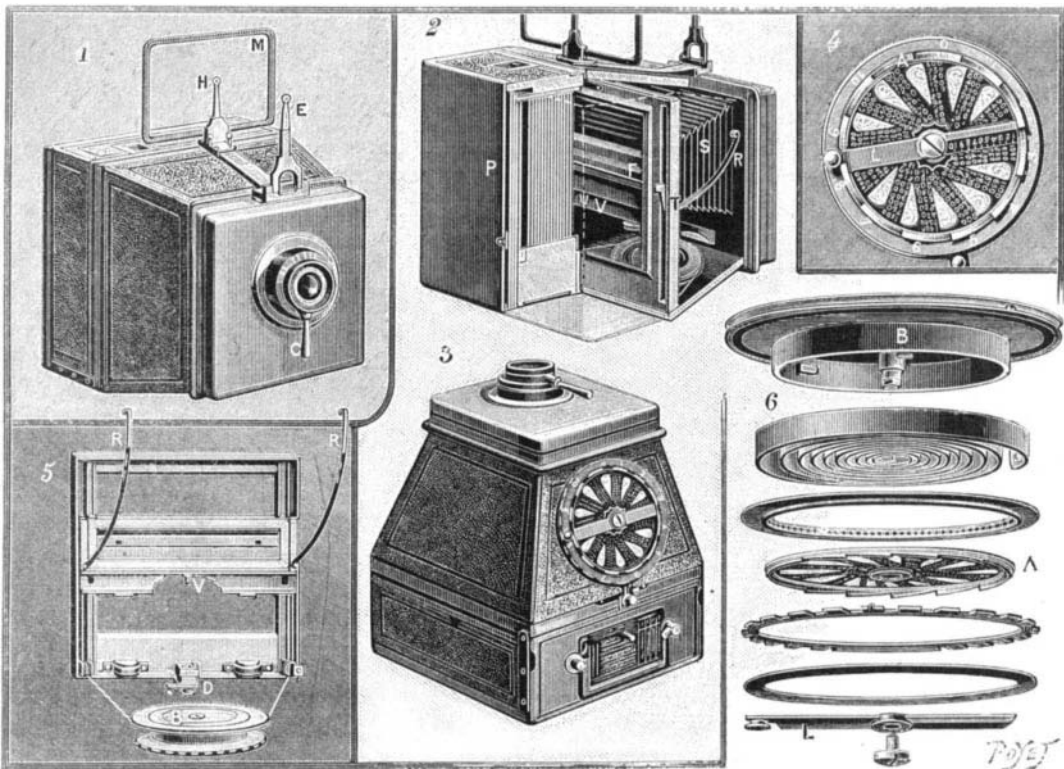
FIG. 4.—SIGRISTE PHOTOGRAPHIC APPARATUS.

No. 1.—General view of the camera and finder. No. 2.—Details of the magazine and shutter slit. Nos. 3 and 4.—View of the apparatus and the dial indicating the velocity. No. 5.—Details of the shutter.