# REVIEWS.

## ON RECENT PROGRESS IN PHOTOCHEMISTRY.[1]

The term '' photochemistry,'' as we intend to treat it, is to be taken in a broader sense than that which is usually accorded to it. It is proposed to express by it more than the influence which light exerts in stimulating chemical activity. The chemical manipulations, reactions, and general manifestations are all instrumental in bringing about the visible effects of this action and should not be isolated from it in treating the subject.

Let us confess at the outset that the influence which light exerts upon silver haloids is still enigmatical. We cannot even to-day say positively what occurs in this case, chemically speaking. It cannot be said without decisive proof that a subhaloid or a perhaloid has been produced, nor can we prove that silver has been reduced to the metallic state.

We may perhaps be permitted to suppose a transformation of the vibrations which we call light into those which may be called chemical vibrations.

When light vibrations impinge upon a mixture of hydrogen and chlorine, it is surely not merely havoc which results, but a rythmic system is produced. With bromine and hydrogen this action takes place in a similar manner, but at higher temperatures. Heat vibrations as well as light vibrations are here perhaps transformed into chemical vibrations.

It requires great strength of scientific faith to believe that in all these actions the light vibrations play merely the part of that famous tip of an eagle's wing, which, accidentally disturbing the repose of a snowflake, causes the avalanche to proceed upon its destructive path downward into the valley.

That light vibrations on impinging upon a chemical compound, such as silver bromide, turn latent within this compound without really decomposing it, has long since been virtually shown by the fact that those parts of a photographic dry plate, thus affected, really exhibit this condition by the readiness with which they are attacked by reducing agencies, suitably applied. This manner of looking at the developing of a photographic negative has never as yet been attempted, or if so, not to our knowledge.

This conception is in no way rendered invalid by the recent observation of T. Sterry, that an exposed but not developed dry plate may be freed from unchanged bromides by immersion into

sodium hyposulphite solution, and after this has been done it may be developed in gaslight by a developer containing silver nitrate.   Sterry assumes that in reality two latent pictures exist within the exposed film, the first of which he calls the inorganic, the second, just mentioned, the organic one.   If our own conception is upheld this differentiation would be needless, because the hyposulphite solution does not dissolve the parts of bromide that had been altered, perhaps by reason of changed stress within the molecule.

The following facts pointing in the direction of the views above stated may be cited :

Attention in the first place is called to the well-known appearances concerning phosphorescence paint.   It is impossible to believe that the light vibrations are merely "bottled up" within the luminous paint, for the light given off is never of the same quality as the light received.

A very simple experiment shows this : A glass plate, upon which a smaller ruby glass plate is allowed to rest, is coated with luminous paint and exposed to sunlight.   After some time the plates are taken into a semi-dark room, and we observe, on removal of the ruby glass, that the part which has been covered appears bright lemon-yellow, while the rest of the plate shines with its peculiar lavender-colored hue.

The red waves have in this instance been changed into yellow ones.   Or, if the ruby glass should have allowed yellow waves to pass through (which, however, is not likely) we must conclude that the red waves had been absorbed.

If we use for the purpose of expressing the difference of color between the light received and that emitted the terms, borrowed from electric terminology,[1] "step-up," and "step-down," we have in our experiment, just described, to do with a "step-up."   With blue glass, under similar conditions, we obtain a more reddish yellow, a "step-down."

In order to show how the vibrations communicated in some way to the phosphorescent plates may be made to further exert their activity, I shall now refer to the experiments of Prof. Zenger, director of the observatory at Prague.   Zenger exposed a phosphorescent plate in a camera, provided with a prism, to the solar spectrum.   He obtained a picture of the same in its entire length, from ultra-red to ultra-violet.   We may remark incidentally that Fraunhofer's lines appear on the phosphorescent plate as bright lines in the red and as dark lines in the violet part of the spectrum.   Zenger proceeded then to face the phosphorescent plate in a printing frame, in the dark room, to a sensitive dry-plate.   Later on he developed the dry plate and thus obtained a permanent picture of the spectrum.

[1] See W. Goold Levison : On a system of classification of luminescent substances, New York Academy of Sciences, December 5, 1898.

In speaking about phosphorescence we must not forget to call attention to the recent research of Wiedemann and his co-workers. The facts most interesting to us about these observations are those of transformation of radiant energy into chemical energy and vice versa of chemical into radiant energy. Wiedemann introduced a new terminology for the generic word phosphorescence. He calls all the pertaining phenomena collectively "luminescence," of which phosphorescence is only a special case.

We may call the fact of a body becoming luminous 'normal' if primarily the oscillations caused by the agency of heat are increased to such a degree, that different oscillations, which we recognize as light, are produced. But besides this kind of generation of light we know another one in which external causes, without corresponding increase of temperature, produce light. This second kind of exciting light Wiedemann calls luminescence.

Photoluminescence is then produced by light as an impinging cause. This, according to its persistence or to its instantaneous appearance, has to be termed phosphorescence or fluorescence. Electric discharges, causing light appearances in gaseous bodies, produce electroluminescence. We notice that Wiedemann found that even here the temperature lies frequently far below the temperature sufficient to cause the incandescence of such gases.

Light caused by certain chemical processes is called " chemiluminescence;" that produced by gentle warming, *e. g.*, of fluorspar "thermoluminescence." Light appearances caused by friction are called " triboluminescence ;" by crystallization are called " crystalloluminescence ;" and by solution, "lyoluminescence."

Without attempting to enter in detail upon this new and interesting field of study we allow our attention to be drawn to some experiments of chemical interest. Lenard and Wolf found that if a photographic negative, newly developed by means of (potash) alkaline pyrogallol and sodium sulphite, is slightly washed and then put into the alum-bath, in the dark, that in the first instance the plate and subsequently the entire bath appear highly luminous. They observed the phenomenon in developing a stellar photograph and sought for the cause. Chandler supposed the sensitive film to be the cause. Phosphorescence, induced by alumina precipitated by potash, was excluded. A true chemiluminescence was found to obtain. This luminescence, however, did not take place if alumina was not precipitated. We know that an excess of potash as well as of alum may prevent such precipitation. On the other hand, precipitation was not always accompanied by luminescence. If sodium sulphite or

pyrogallol were left out of the solution, the most perfect precipitation without luminescence occurred.

In short, though the proportions of the developer were changed in many ways it was not only shown that sulphite must not be present in excess nor in too small quantities (above 1.25 per cent. or below 0.13 per cent.), in order to produce the effect ; in the same way an excess of pyrogallol above 0.3 prevented it, but 0.005 per cent. pyrogallol sufficed to produce it.    Evidently, in order to successfully perform the experiment, a fifth substance, not intentionally introduced into the developer, was at work right along.    Observation showed that the precipitated aluminum hydroxide after luminescence had occurred, had carried down all the pyrogallol, the supernatant liquid was colorless, the precipitate yellow.    Suspicion was aroused that alumina, in its finely divided condition, had fixed upon its surface not only all of the pyrogallol but also oxygen, which was proved to be the sought-for fifth substance.    The luminescence was the consequence of a sudden energetic oxidation of pyrogallol.

The proof was rendered in many ways.    The experiment was performed in presence and in absence of air.    In the first case luminescence occurred, in the latter not.    A further experiment was performed in presence of oxygen, when luminescence appeared brighter than ever.

A conundrum, however, was offered in the fact that sodium sulphite, an oxygen consumer, purposely added to developers to prevent spontaneous oxidation of pyrogallol ($e. g.$) was nevertheless necessary to bring about the phenomenon.

The curious fact was experimentally established that the pyro-sodium sulphite potash developer used up oxygen less swiftly than did pyropotash alone, thus the developer containing sulphite remains richer in free oxygen than without it.

This is one example of true chemiluminescence caused by oxidation of pyrogallol.

Another, still more interesting, example of chemiluminescence is offered by the appearance of what was formerly called " sea-phosphorescence."    This luminous appearance of the ocean, according to newer researches of Otto, is the consequence of oxidation of organic matter by means of ozone.    Water, introduced together with ozone into the apparatus shown in the accompanying figures, will turn highly luminous upon agitation.    Distilled water will not show the effect, but upon addition of urine, alcohol, benzene, or other suitable oxidizable material, luminosity will appear.

It may be of use to those present interested in photography, to say a few words about the changes in developers.    There is in the first place a developer to be mentioned, producing color tones in dia-positives for the purpose of projections.    We all

know how important a factor is the suitable color for a given picture.

Silver chloride gelatine plates should be used (similar to the mixture on the Aristo papers) and the plates are not printed out under the negative. The outlines of the picture must faintly
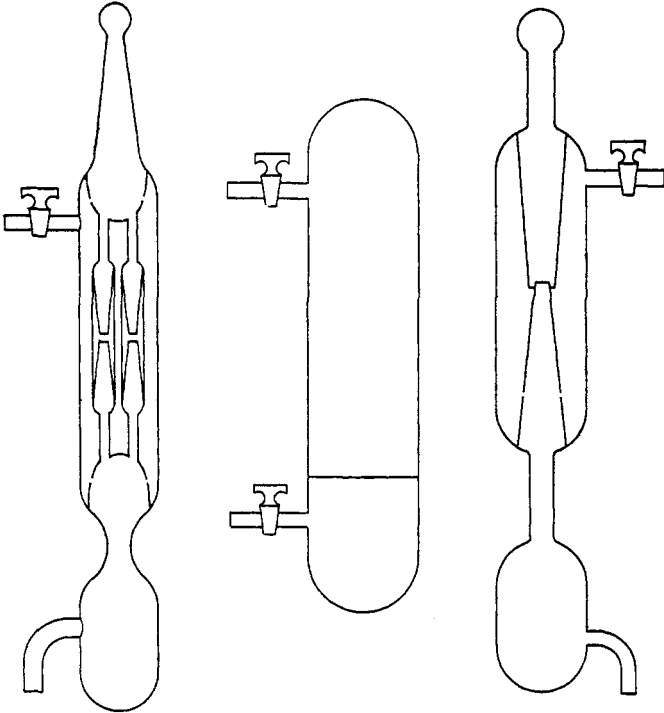
show in daylight, to which they should be exposed for one to three minutes, according to the kind of light and of the negative. As a uniform developer, paramidophenol is recommended by Hanneke, of the Berlin-Charlottenburg photochemical laboratory.

Distilled water ..................... 1000 cc.
Crystallized sodium sulphite ....... 50 grams
Citric acid ........................ 8 "
Paramidophenol hydrochloride..... 7 "

In this manner pictures in yellowish-brown tints are obtained; carmoisin, violet to steel blue tints, are produced subsequently in a gold-bath containing ammonium thiocyanate. Acetone and aldehyde are beginning to take the place of alkalies in our

developers.    The brothers Lumière and Seyewetz were the first
to recommend these substances.

Water ......  ......................... 500 cc.
Sodium sulphite (double usual amount
   to produce black tone) ............ 200 grams
Concentrated  sulphuric acid......... 10 drops
Pyrogallol ......  .................... 14 grams

Fifteen cc. of this and five cc. acetone and dilution to 50–120 cc.
with water.  Excess of acetone produces a greenish color.  Ace-
tone is said to harden the film.   Consequently this developer is
of importance for photographic work in tropical climates.   It is
not necessary to use C. P. acetone but the commercial product
of boiling-point $+56°–58°$ C., which costs about thirty cents per
pound, suffices.

Bromide paper developed with acetone developer will be found
free from blisters.   The aldehyde developers, in contrast to the
acetone developers, are rapid workers and they require an ample
addition of potassium bromide.

Water.............................. 100 cc.
Sodium sulphite..................... 15 grams
Formaline (forty per cent.).......... 2 cc.
Hydroquinone............... ....... 1.5 grams

Ordinary ethyl aldehyde (fifty per cent.) can be used also,
while benzaldehyde, acetophenone, and benzophenone, which
can only be used in alcoholic solution, are practically useless.
Dr. Andresen furnishes a list of reactions of the current develop-
ers.    He includes in his list the following :

Amidol = Hydrochloride of 2,4-diamidophenol.
Eikonogen = $\alpha$-Amido-$\beta$-naphthol-$\beta$-sulphonic acid.
Glycin = $p$-Oxyphenylglycin.
Hydroquinone.
Metol = Methyl-$p$-amidophenyl sulphate.
Ortol = Methyl-$o$-amidophenol sulphate, mixed  with
                   hydroquinone.
Paramidophenol hydrochloride.
Pyrogallol.

In regard to the use of formalin for photographic purposes it is
a fact worth  recording, that the expansion of paper, conse-
quently any distortion whatever of the picture, may be avoided
by previous immersion of the paper in  a  two per cent. formalin
solution and subsequent drying.

The sensational news, which passed some time ago through
our  daily papers, embellished by appropriate pictures, sugges-
tive of spiritistic productions, were based  upon the observation
of Dujardin, that imprints of the human hand  may be produced

within the developing bath upon dry plates. It was found that the animal heat produced these pictures and that a direct contact of the plate with the hand, only shielded by another glass plate, is necessary. If the covering glass plate was separated from the dry plate (both in the developer) by means of glass rods or glass cubes, no action occurred.

It is gratifying to the chemist to observe how chemistry enters in almost every direction as a handmaid into practical photochemical pursuits.

Lieutenant Kiesling has constructed a magnesium light apparatus, avoiding the smoke attending the use of this element. He allows salt-mouthed vials of 250-400 cc. capacity filled with dry oxygen (directly from the gasometer), and containing magnesium ribbon and a fuse, or an electric wire system, to oscillate like a pendulum. The bottom of the little vials is covered with a small quantity of plaster of Paris or asbestos. It is said of magnesium burnt in oxygen that it furnishes a light the actinic action of which is twelve times as great as if burned in air. The little vials remain useful for twenty-four hours. Acetylene light has also been recommended.

Dr. Roberts, Director of the Archæological Museum in Halle, observed that in a collection of silver coins of the fifth century B. C. (Tetradrachms) had suffered a change on the surface of the side exposed to light. The analysis of the thus changed surface proved this to consist of silver chloride. An attempt is made to explain this by showing that these coins had for centuries been resting in sand containing NaCl. A coinage from silver containing silver chloride is excluded since the interior parts of the coins were proven to consist of tolerably pure silver.

A comparatively new field of research is opened up by the study of what makes an organic substance a developer. What are the groups with developing functions? A. and L. Lumière and Seyewetz have studied the influence in this direction of alkyl-substitutions in groups possessing developing functions.

As a general rule it has been granted that the faculty of developing the so-called latent picture, exists in compounds containing at least two hydroxyl groups in ortho or para position.

These authors have studied the para-compounds of amidophenols and of polyamines for which the above rule was still under discussion.

Paraphenylendiamine and paramidophenol were subjected to alkylization, and the following substitution-products were prepared and tested in regard to their developing properties:

1. Monomethylparaphenylenediamine, $C_6H_4\begin{cases} NH.CH_3 \ (1) \\ NH_2 \quad (4) \end{cases}$
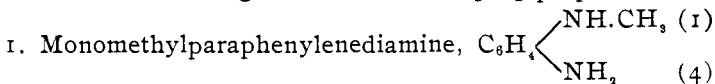
2. Dimethylparaphenylenediamine, $C_6H_4 \begin{cases} N(CH_3)_2 \ (1) \\ NH_2 \quad (4) \end{cases}$

3. Tetramethylparaphenylenediamine, $C_6H_4 \begin{cases} N(CH_3)_2 \ (1) \\ N(CH_3)_2 \ (4) \end{cases}$

4. Monomethylparamidophenol, $C_6H_4 \begin{cases} OH \quad (1) \\ NH.CH_3 \ (4) \end{cases}$

5. Dimethylparamidophenol, $C_6H_4 \begin{cases} OH \quad (1) \\ N(CH_3)_2 \ (4) \end{cases}$

6. Paranisidine, $C_6H_4 \begin{cases} O.CH_3 \ (1) \\ NH_2 \quad (4) \end{cases}$

The compounds 1 to 5 are developers. 1 to 3 may even be used as such without the addition of alkali. 6 was without developing power.

The alkylization, as far as shown, therefore, does not destroy the developing power. We must remember that the alkyl-substitutions into an amido group weaken its basic properties but do not entirely destroy them. On the other hand, if a hydroxyl of a phenol suffers alkylization the phenol properties are lost entirely (as·in 6), as are the acid properties in most neutral salts, and the developing power is correspondingly lost.

Leaving the chapter of the chemistry of developers we record a number of various items of general interest.

Glycerol has been successfully used instead of alum in electric light projection. The lenses as well as the diapositives are endangered by the high temperature of the arc light. For the celluloid films of the kinematograph this danger is obvious. The alum cell heretofore used is sometimes brought up to boiling and in the best case it will form bubbles. Glycerol has been used even between the source of light and the condensing lens. After a performance of two hours under these conditions with an electric lamp of 2000 candle-power, the glycerol (which does not form bubbles and boils at $+290°$ C.) registered $+80°$ C. Pure glycerol being practically colorless, the light is not in any way weakened.

Talking about the kinematograph, it may be worth while reminding this audience of the immense proportions which the applications of photochemistry have assumed in this country. Mr. Dunn ordered from the Eastman Co. three kinematograph films, each 50,000 feet long. Each film was said to cost $10,000. The films were intended to be used at the occasion of the Corbett-McCoy contest in Buffalo, and three apparatus to work

simultaneously in order to secure at least one good copy. Each film of 50,000 feet was supposed to run for eighty minutes (625 feet per minute) and twenty-seven pictures were to be taken per second.
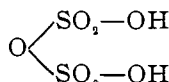
The use of the most varying chemicals for photochemical pursuits is surely on the increase and it happens frequently, as we stated at the outset, that the chemist is confronted with reactions quite difficult to understand.

A case of this kind is offered in the use of ammonium persulphate for the purpose of softening hard negatives. This technical term means, in common language, that a negative which shows too strong contrast between high lights and shadows has to be brought down to more uniform delineation by chemical action. Mechanical rubbing down of the denser parts by means of alcohol, or local or entire reduction (as it is styled) by means of potassium ferricyanide and sodium thiosulphate, were tedious and sometimes doubtful modes of procedure.

The ammonium persulphate in a five per cent. aqueous solution has the faculty of attacking the denser parts, without injuring the detail in the shadows of the negative. Ammonium persulphate is a salt of persulphuric acid. We are in this instance agreeably reminded of Kekulé's lucid way of showing at a glance the similarities in the constitution of compounds.
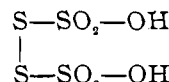
$$O \Big\langle \begin{matrix} H \\ H \end{matrix}$$

Water.

$$O \Big\langle \begin{matrix} SO_2-OH \\ SO_2-OH \end{matrix}$$

Disulphuric acid (or pyrosulphuric acid).

$$\begin{matrix} S-H \\ | \\ S-H \end{matrix}$$

Hydrogen persulphide.

$$\begin{matrix} S-SO_2-OH \\ | \\ S-SO_2-OH \end{matrix}$$

Tetrathionic acid.

$$\begin{matrix} O-H \\ | \\ O-H \end{matrix}$$

Hydrogen peroxide.

$$\begin{matrix} O-SO_2-OH \\ | \\ O-SO_2-OH \end{matrix}$$
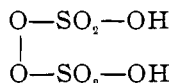
Persulphuric acid.

The acid itself has not been prepared, but its salts are in use as oxidizers. They are mostly prepared from ammonium persulphate, which is obtained by electrolysis of ammonium sulphate.

The action of ammonium persulphate upon a negative is still under discussion. While some claim that a soluble double salt, $NH_4O.SO_2.OAg$, is formed, others assert that ozone is generated, as with hydrogen peroxide.

There is a chance for still further study. We cannot conclude this brief summary without referring to the action of most varying substances upon dry plates. Not only do certain vapors, but also matter from which no material vaporization can otherwise be noticed, attack the sensitive film of a photographic plate.

Messrs. Muraoka and Kasuya, in Kyoto, Japan, made a study of the light of glow worms. In addition, they experimented in the direction just now referred to. I quote their own words : '' We also experimented with magnesium oxide and cadmium oxide. The first has no action, but the latter shows a curious behavior, inexplainable either by radiation or vaporization. We took two thick pieces of card-board, A and B, both of the size of a photographic dry-plate ; from the center of A we cut out a small square and from that of B a large square. A was put upon a glass plate and the square cut away was filled with powdered cadmium oxide. Then A was covered with B and the dry-plate was put on top of B. We expected to find that the plate would be attacked all over the area of the larger square of B, since the vapor from the smaller opening could have easily spread to the edges of the larger square. But on developing the plate it was found that the blackening was restricted to the size of the smaller square.

If A is separated from B to the distance of 1 cm. and a copper wire is stretched between the two without touching them, no blackening will be produced above the copper wire. According to this, a radiation appears to be at work, but it remains inexplainable why this radiation does not also obliquely extend to the larger square.''

It may interest you to hear of experiments performed by myself with the view of practical application. I faced daguerreotypes to dry-plates in a printing frame and obtained faint but very clearly outlined copies. These copies became more distinct, very likely by contrast, when I exposed the frame to light, the dry-plate being thus blackened to the extent of about two inches all around the impression made by the daguerreotype.

*References :* Photographische Mitteilungen, January, 1898, to November, 1898.
Annalen der Physik und Chemie, 64, No. 1 (*1898*) ; 34, No. 7, (*1888*); 34, No. 8b (*1888*).

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