BIOGRAPHICAL MEMOIR

OF

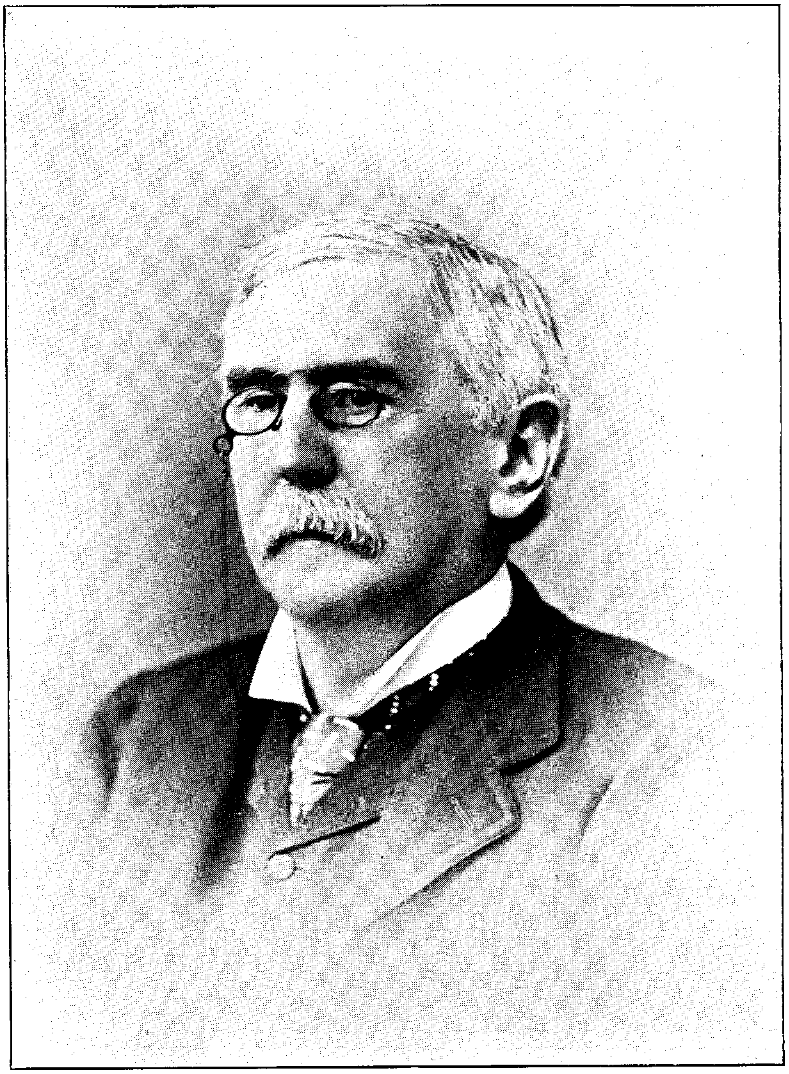
MATTHEW CAREY LEA.

1823-1897.

BY

GEORGE F. BARKER.

READ BEFORE THE NATIONAL ACADEMY OF SCIENCES,
APRIL 21, 1903.



M. Carey Lea.

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Perhaps there is no department of physical science whose seductions are more alluring or whose results are more fascinating than that of chemistry. The nature of matter has always been, even from the earliest times, one of the most favorite speculations of the human mind; and the study of the relations of the molecule to the atom, and therefore of the part which these minute portions of matter play in natural phenomena, has ever been one of the most interesting subjects for research. In no department of these so-called matter-sciences, however, has more original and suggestive work been done probably than in that of photographic chemistry, based as it is so largely upon the nature of the metal silver; and no investigator apparently has added to our knowledge more valuable facts in this direction than our late worthy colleague who is the subject of the present memoir.

MATTHEW CAREY LEA was born in Philadelphia August 18, 1823. His father, Isaac Lea, the distinguished naturalist, belonged to one of the old Quaker families of that city, his grandfather, John Lea, who had come to America in 1700 with William Penn, having been eminent for many years as a preacher at the Friends' meetings. His mother was Frances A. Carey, the daughter of Matthew Carey, the eminent and prolific writer on political economy and a publisher of repute. Upon his marriage, in 1821, Isaac Lea became a member of the publishing firm of M. Carey & Sons, in which he continued as an active partner for more than thirty years. He early became interested in science, devoting himself to natural history, and especially to conchology. His "Observations on the Genus Unio," 1827–1874, fill thirteen quarto volumes, containing two hundred and eighty plates. His investigations extended also to geology, mineralogy, and paleontology. He became a member of the Academy of Natural Sciences in Philadelphia in 1815, and was chosen its President in 1858. In 1860 he was elected president of the American Association for the Advancement of Science. He died in Philadelphia in 1886, at the age of 95 years, bequeathing his unrivaled collection of shells and minerals to the United States National Museum.

Carey Lea was the second son in a family of three sons and a daughter, the eldest son dying in infancy. His younger brother, Mr. Henry C. Lea, the well-known publisher and a writer of great eminence on philosophical and historical subjects, is still living in Philadelphia.

Trained amidst such scientific surroundings, it is not surprising that our late fellow-member early developed a decided taste in this direction. But as his constitution was never a vigorous one, he was sent neither to school nor to college, but spent the early part of his life at his home, where he was given a very broad and thorough education by the best private tutors procurable. In this way his strong intellectual powers and retentive memory enabled him to acquire a culture of great value, especially in languages, in literature, and in the natural and physical sciences. His father's scientific eminence, coupled with the possession of ample means, greatly facilitated the development of his powers. In 1832, at the age of 9 years, he spent six months in Europe with his parents, where he was brought into contact with eminent men of science, both in England and on the Continent, many of whom had long been friends of his father.

At first his choice was for the legal profession, and he entered the office of the Hon. Wm. M. Meredith, then the leader of the Philadelphia bar. After the completion of his studies he was admitted to practice about the year 1847. Continued ill health, however, the result of overstudy, forced him not long afterward to abandon the profession of the law. He went again to Europe, where he spent some years in hope of permanent relief, but without success. From that time he remained more or less an invalid, having repeated attacks of illness, which largely incapacitated him for the more active pursuits of life.

His great interest in scientific matters, and especially in chemistry, led him, not long after his return from Europe, to enter the laboratory of Professor James C. Booth, where he acquired that proficiency in chemical science and that love of research which distinguished him ever afterward. His later experimental work was mainly done in the private laboratory at his home in Chestnut Hill. His more important papers, a list of the titles of which is appended to this memoir, number about one hundred, the most of which appeared in the *American Journal of Science* during the years from 1860 to 1897. But his minor papers, especially those on photography, published in the technical journals, far exceeded this number. Those in the *British Journal of Photography* alone number nearly three hundred.

Matthew Carey Lea's earliest scientific paper was entitled "On the First or Southern Coal Field of Pennsylvania." It appeared in 1841 in the *American Journal of Science and Arts*, and contains the results of his proximate analysis of fifteen authentic samples of Pennsylvania coal, these analyses having been made in Professor Booth's laboratory. The easternmost coal examined was from the Lehigh region. It contained 87 per cent. of carbon, 7.30 per cent. of volatile matter, and 5.70 per cent. of ash. The westernmost came from Rattling Run Gap, and consisted of carbon, 76.10 per cent., of volatile matter, 16.90 per cent., and of ash, 7 per cent. The highest percentage of fixed carbon in these coals was contained in that from Tamaqua, 91 per cent. The lowest was in that from Yellow Springs Gap, 74.70 per cent. These analyses were made with the object of testing the truth of an opinion expressed by his father, that "the hard or highly carbonized anthracite of the eastern end of the southern coal field changes to the bituminous in the western end by nearly regular gradations." "It would appear from these results," he says, "that the bituminous qualities of the coal increase with considerable regularity from Tamaqua to Rattling Run."

The purely chemical investigations of Carey Lea, both in organic as well as in inorganic chemistry, covered a wide range of subjects. Like many others, he indulged in speculations on chemical theory, especially upon the connection between the properties of the atoms and their numerical relations. In the first part of his paper "On Numerical Relations existing between the Equivalent Numbers of Elementary Bodies," he undertook to show "that the number 44.45 plays an important part in the science of stoichiometry, and that the relations which depend upon it are supported, in some cases at least, in a remarkable manner, by analogies of atomic volume." Since solids and liquids are very far from being governed in their volume combinations by the simple laws which control gases, we may expect, if occasionally we find such a coincidence, to observe a close relationship between the substances thus united. But more than this: If, for example, we find that a given volume of silver unites with a given volume of oxygen, and that the same volume of gold unites with precisely the same volume of oxygen, we may "conjecture that gold may differ from silver only by a third substance which unites with the silver without increasing its volume or affecting the amount of oxygen which it is capable of saturating, but which, on the other hand, alters its chemical equivalent, its specific gravity and other physical characters." Further, "if we find that by subtracting from the chemical equivalent of silver half the difference between the equivalents of silver and gold, we obtain the equivalent of a third metal, copper (Cu=63.4), which also, under equal volumes, combines with a quantity of oxygen expressed by a very simple relation with that capable of saturating gold and silver, we may at least speculate that the three may form a series consisting of two substances combined in different proportions." His numerical computations show that the relation spoken of extends to no less than forty-eight of the elementary bodies.

In the second part of this paper a new and wholly distinct relation is pointed out, which the author calls a relation of "geometrical ratios" to distinguish it from the relation of arithmetical differences discussed in the first paper. Their nature consists in this: "that if we take two substances and examine the ratio which subsists between the numbers representing their atomic weights, we may find in certain cases that it is identical with the ratio subsisting between the atomic weights of two other substances." Thus the ratio between the atomic weights of oxygen and nitrogen, for example, is that of four to seven, which is exactly the same as that between those of zirconium and potassium and those of potassium and barium.

In July, 1864, Mr. Lea published two papers on the Platinum group, the first being entitled "Notes on the Platinum Metals and their separation from each other," and the second "On Reactions of the Platinum Metals." The material used was California osmiridium, and was obtained from Professor Booth, of the United States Mint. By following substantially the process of Claus, three portions were obtained: (*A*) a sandy crystalline precipitate of iridium sal-ammoniac, (*B*) a liquid obtained by washing this precipitate with saturated solution of sal-ammoniac, which carried through nearly the whole of the ruthenium as bichloride, and (*C*) another liquid obtained by using dilute solution of sal-ammoniac in the washing, and which contained, besides some ruthenium bichloride, small quantities of iridium and rhodium. In treating the portion (*A*) it was placed in a large flask, with twenty or twenty-five times its weight of water, and heated to boiling. Then crystals of oxalic acid were added; whereupon effervescence took place, and the iridium salt was rapidly reduced. On standing for a few days, after adding sal-ammoniac crystals to the boiling solution, the platinum sal-ammoniac separated as a crystalline powder. The mother liquor was then boiled with aqua regia, and, on cooling, the iridium sal-ammoniac crystallized out pure. This use of oxalic acid for purifying the double chloride of iridium and ammonium is here proposed for the first time and possesses marked advantages over the older methods. Its reducing action upon iridium bichloride at the boiling point is immediate, while it has no effect on the bichloride of ruthenium, and leaves the platinum in the condition of double chloride, remaining behind as a reddish powder. The paper discusses the reactions of caustic baryta upon iridium, and points out the marked difference between the action of this substance and that of the alkalies upon the platinum metals. It also calls attention to a new reaction for ruthenium, first observed by the author. When a solution of hyposulphite of soda is mixed with ammonia and a few drops of sesquichloride of ruthenium solution is added, a magnificent red-purple liquid is produced, which, unless quite dilute, is black by transmitted light. On testing the sensibility of this reagent it was found that $\frac{1}{5000}$ of the sesquichloride gave a bright rose purple, $\frac{1}{20000}$ to $\frac{1}{30000}$ a fine rose color, $\frac{1}{50000}$ a paler but still perfectly distinct color, and $\frac{1}{100000}$ a still paler but unmistakable rose tint. The chief value of this new test for ruthenium, the author says, lies in the fact that it is capable of detecting ruthenium in presence of an excess of iridium. No precautions are necessary, and the reaction is always obtained with the greatest facility.

In the second part of this paper Mr. Lea describes the reactions of hyposulphite of soda with the other platinum metals, and also gives the effect of the presence of these metals upon the ruthenium reaction. Even when iridium is present, the hyposulphite test is at least ten times more delicate than any other. Platinum in small quantities is without effect, and in larger quantities only changes the color from a rose to a wine red. Evidently this test is a valuable one for the purity of iridium. If the suspected iridium salt be boiled with hydrochloric acid, and ammonia added until the liquid assumes a pale olive color, then, on adding the hyposulphite and boiling, any increase of color indicates the presence of impurity. If the liquid acquires a rose color, ruthenium is present; if a wine color, platinum is probably present; and if brown, palladium is indicated. The paper concludes with a discussion of the reactions of the platinum metals with tetrathionic acid, with sulphate of quinia, with protochloride of tin, with ammonio-chloride of zinc, with ferrocyanide of potassium in caustic soda, and with Schlippe's salt. For ruthenium sesquichloride, the reaction with hyposulphite is characteristic; for the bichloride, that with ammonio-chloride of zinc, giving a rose-colored precipitate, is distinctive; for iridium the best test is the protochloride of tin and potash, and for palladium the reaction with tetrathionic acid is highly characteristic.

Conversely, the author has suggested ruthenium sesquichloride as a reagent for the detection of sodium hyposulphite. He has shown that a solution containing one four-thousandth of hyposulphite, when boiled with one of the ruthenium compounds made alkaline with ammonia, gives a clear rose-red color; one twelve-thousandth gives a well-marked pink liquid, and one containing one twenty-five-thousandth gives a salmon color.

In 1866 Mr. Lea called attention to the great increase of delicacy which is produced in the starch reaction for iodine by adding chromic acid to the solution. After adding the starch to the suspected liquid, add a drop or two of a dilute bichromate solution and then a few drops of hydrochloric acid. With solutions of iodide of potassium of $\frac{1}{100000}$ the blue precipitate is abundant, and indications are observable at $\frac{1}{400000}$, though at $\frac{1}{800000}$ the result is somewhat doubtful.

Carey Lea described, in 1874, a new compound formed by the union of mercuric iodide with silver chloride, analogous to the double iodide of mercury and silver, and that of mercury and copper, which had already been obtained by Meusel. By adding to a weighed quantity of potassic iodide in solution an exactly equivalent quantity of mercuric chloride, agitating and allowing the precipitate to settle, and then adding an equivalent quantity of silver nitrate solution, three precipitates appear in the liquid—scarlet mercuric iodide, white silver chloride, and the yellow body which results from their union. After thorough admixture and after standing for twenty-four hours, the new compound appears as a heavy yellow powder, wholly free from any trace of red and inclining to a greenish or lemon-yellow color. Mixed with gum and spread on card-board, it dries to a full chrome yellow. The substance exhibits remarkable properties in its relations to heat. Even below 100° F. it begins to redden, and the color increases up to about 140°, when it has a bright scarlet color, resembling vermilion. On cooling, its natural color returns. The author does not agree with Meusel in the opinion that these substances are mechanical mixtures. He believes them to be true chemical compounds, though perhaps rather loose ones.

A paper by Carey Lea, "On the Nature of Certain Solutions and on a New Means of Investigating Them," was presented to the National Academy of Sciences at its April meeting in 1893. In this paper he pointed out that two classes of salts are formed by the three best known acids; the one perfectly neutral, like the alkali salts, the other decomposed by water like mercuric sulphate, bismuth nitrate, and stannous chloride. In the case of the sulphates, the number of metallic salts which have a neutral reaction is comparatively small. The question now is as to the meaning of the acid reaction of sulphates. Is free acid present in any or all of the cases? The unreliability of the ordinary tests for free sulphuric acid led the author to devise a new reaction by means of which the condition of such solutions may be examined and free sulphuric acid be detected in the presence of sulphates with great accuracy and sharpness, even when only a trace is present. The new method is based on the fact that from the sulphate of iodo-quinine, the well-known polarizing salt discovered by Herapath, it is possible to remove the whole of the sulphuric acid without breaking up the molecule. This may be done with either the carbonate or the hydroxide of barium, by placing this in a beaker, covering it with about 70 per cent. alcohol, and dropping into it the crystallized herapathite. In presence of the barium compound it dissolves readily and freely, forming a deep sherry-wine colored liquid, which, when allowed to dry spontaneously, leaves an amber-colored varnish without a trace of crystallization. If, however, a minute quantity of sulphuric acid be added to the solution, there is left behind, on evaporating it, a characteristic bluish black film with isolated crystals of iodo-quinine sulphate. When barium carbonate is used in the preparation—and it is preferable—some evolution of carbon dioxide occurs; whence it seems probable that the resulting solution contains a free base. From this solution the sulphate is readily regenerated by free, but not by combined, sulphuric acid. Even neutral sulphates of weak bases, like quinine and brucine, are wholly without action. From an extended investigation of the conditions, the author concludes: (1) that the solution of iodo-quinine affords the means of detecting free sulphuric acid even in traces, in presence of combined sulphuric acid; (2) that the salts of protoxides of the heavy metals do not owe their acid reaction to dissociation. With one exception, the solutions of their sulphates contain no free sulphuric acid. This exception is ferrous sulphate, whose solutions always contain free acid. (3) That sesquisulphates are always dissociated in solution; (4) that alums, with the exception of chrome alum, are always dissociated in solution; and (5) that acid salts are dissociated in solution; sometimes perhaps completely.

The following year another noteworthy paper by Carey Lea was communicated to the National Academy, entitled a "New Method of Determining the Relative Affinities of Certain Acids." This method was based on the principle that "the affinity of any acid is proportionate to the amount of base which it can retain in the presence of a strong acid selected as a standard of comparison for all acids." Suppose, for example, that sulphuric acid is taken as the standard, the quantity employed being always a gram-molecule at a fixed rate of dilution. Evidently two gram-molecules of sodium hydroxide would exactly saturate it. Taking, now, any given acid, it may be that the quantity of its sodium salt corresponding to three gram-molecules of sodium hydroxide exactly extinguishes the reaction of one gram-molecule of free sulphuric acid, the presence of the standard acid in the free state being ascertained by the herapathite test already mentioned. Suppose, now, that with a second acid we find that a quantity of its sodium salt corresponding to four gram-molecules of the hydroxide is needed to extinguish the sulphuric reaction. Then it follows that the affinity of the second acid is exactly twice as great as that of the first. At the point where the free sulphuric acid reaction was extinguished, the second acid retained twice as much sodium as the first, and this quite independently of any question of comparative basicity. Thus in the case of hydrochloric acid there was needed as a mean 29.37 gram-molecules of sodium chloride to extinguish the reaction in one gram-molecule of sulphuric acid. At this point the solution necessarily contained

$$Na_2SO_4 + (HCl)_2 + 27.37\ NaCl,$$

as is proved by the fact that the solution gives no longer a trace of free sulphuric acid reaction. Hence 27.37 gram-molecules of sodium chloride is the proportion of undecomposed sodium chloride that must remain in the solution in order that the sulphuric acid may be completely converted into sodium sulphate, and may remain as such in the solution in a condition of equilibrium. The number 27.37 therefore represents the strength of the affinity of hydrochloric acid for sodium. To compare acids of different basicities, however, it is convenient to refer them all to dibasic sulphuric acid, and therefore to divide this number by two; so that 13.68 may be taken as the index of the affinity of hydrochloric acid.

For pyrophosphoric acid, the mean value found for the quantity necessary to extinguish the free sulphuric acid in one gram-molecule of sulphuric acid was found to be 0.963 gram-molecule of sodium pyro phosphate. Hence at this point the liquid contains

$$Na_2SO_4 + \tfrac{1}{2}\,(H_4P_2O_7) + .463\ (Na_4P_2O_7)$$

in equilibrium. The number .463 therefore represents the comparative affinity of pyrophosphoric acid, except that as this acid is tetrabasic, it must be multiplied by two in order to bring it into comparison with dibasic acids. The index of pyrophosphoric acid is therefore .926; so that half a molecule contains the quantity of sodium required to saturate a molecule of sulphuric acid, and therefore only half a molecule of pyrophosphoric acid is set free. In other words, it is found by experiment that the quantity of pyrophosphate necessary to extinguish the reaction for free sulphuric acid with 1,000 molecules of that acid is 963 molecules. Out of this 500 molecules of pyrophosphoric acid are set free and there remain 463 molecules of undecomposed pyrophosphate. This number 463 multiplied by 2 because of the basicity of the acid, and divided by 1,000 to make it correspond to one molecule of sulphuric acid, gives .926 as the index of pyrophosphoric acid. The author points out that the state of equilibrium is always conditioned by the degree of concentration; so that if to any solution of sulphuric acid a salt is added in just sufficient quantity to extinguish the sulphuric-acid reaction, the addition of a little water at once changes the equilibrium. A certain portion of the salt added is reformed, and the sulphuric reaction reappears. By means of this method, therefore, it may be shown (1) that when to free sulphuric acid a salt is added in sufficient quantity to cause the whole of the sulphuric acid to saturate itself with the salt-base, it is possible by means of the herapathite test to determine the exact point of such saturation; (2) that a series of equilibria thus obtained with different salts enables us to determine the comparative strength of the affinities of the acids of those salts; (3) that the fact, already proved in other ways, that even small quantities of weak acids added to sulphates will set free a certain quantity of sulphuric acid can, by the means here given, be rendered for the first time visible to the eye by a well-marked chemical reaction.

The same year he proposed two new methods for reducing platinic to platinous chloride—one by the action of potassium acid sulphite, the other by that of alkali hypophosphites. In using the latter method, if the heat is continued after the conversion into the red salt is complete, the solution changes to dark brown, and has properties which seem to justify the assumption that it contains a platinum subchloride. Since silver chloride, after being acted on by light, yields nothing to nitric acid, it cannot have been reduced to metal. The tendency to form subchlorides in the case of both metals seems, therefore, unmistakable.

In Organic Chemistry, as well as in Inorganic, Carey Lea made many valuable investigations. He published very early a series of papers on picric acid and its compounds, giving in the first of these, which appeared in 1858, an important modification of one of the processes for preparing the acid. The yellow Australian gum from the *Xanthorrhea hastilis* is the most advantageous substance from which to prepare picric acid, from which it is obtained by acting on it with six or eight times its weight of strong nitric acid in the cold. In the new process the acid is added at intervals, and the action is moderated by the addition of water, the heat being carefully regulated. In this way the amount of nitric acid required is diminished one-half, and the violent evolution of fumes is avoided. In this paper are described the picrates of barium, glucinum, aluminum, manganese (manganous), iron (ferrous and ferric), cobalt, nickel, chromium (chromous and chromic), zinc, cadmium, copper, mercury (mercuric), silver, urea, and quinine.

In a second paper, read at the Newport meeting of the American Association, he discusses the claim made for picric acid as a test for potash, and shows that an alcoholic solution of picric acid or an aqueous solution of picrate of soda will produce a precipitate in almost any alkali solution, whether of soda, ammonia, or potash, except under circumstances of great dilution. Hence he infers that picric acid is wholly unreliable as a test for potash; in fact, that it is a better test for soda, because with soda solution it yields a precipitate which, when redissolved by heat, gives a characteristic spherically radiated bright canary yellow crystalline precipitate, whereas the precipitate given in a potash solution can never be positively distinguished from that thrown down in a solution of ammonia, the precipitate appearing when only half of one per cent. of the ammonia salt is present.

About the same time Carey Lea published a paper giving the results of his study of the ammonio-picrates, describing the salts of silver, copper, cobalt, zinc, cadmium, chromium, manganese and iron. In a preliminary paper he had shown that when certain metallic salts are precipitated by ammonia in excess, a more or less complete solution of the precipitate takes place. When treated with an alkali picrate, however, the solution yields an immediate precipitate of a compound of the base with picric acid and ammonia. These precipitates are often very beautiful, are generally yellow in color, and are nearly insoluble in water, which readily decomposes them, especially if added in excess.

In 1861 he gave a résumé of his observations on picric acid, considering its solubility in sulphuric acid, the tests for it, the methods of its purification, and the effect of reducing agents upon it. The most delicate tests for picric acid are: 1st, ammonio-sulphate of copper, which gives a greenish crystalline precipitate; 2d, potassium sulphide with excess of alkali, which on heating gives a deep red liquid; 3d, potassium cyanide, which also gives a red liquid on heating. A solution of $\frac{1}{10000}$ part of picric acid in water gives no precipitate with the first test, but responds to the others, the cyanide test being the more delicate of the two.

Mr. Lea subsequently made a number of studies on the ethyl and methyl bases. For preparing ethylamine he advises to mix nitrate of ethyl with its own volume of strong alcohol, and to add an equal bulk of concentrated solution of ammonia. On placing the liquid in strong sealed tubes and heating on the water bath to boiling for three hours, the reaction is completed, diethylamine and triethylamine being formed at the same time. To separate these bases from each other, the author recommends their conversion into picrates, the triethylamine salt being extremely insoluble, the salt of diethylamine extremely soluble, and the solubility of ethylamine picrate intermediate. To separate the bases from ammonia, the mixture is converted into sulphates, the solution is evaporated at 250° F., the pasty mass is exhausted with strong alcohol, and the resulting solution is again evaporated. To separate the bases, the mixed amine sulphates were distilled with caustic potash, the bases obtained were saturated with picric acid, and the solution allowed to crystallize. The first crystals were triethylamine picrate, the second ethylamine picrate, and the third diethylamine picrate, in the order of solubility.

In a paper on the "Reactions of Ethylamine and Diethylamine," the author states at considerable length the effects produced upon these bases by various metallic salts, and also gives the results of some experiments on their isomorphism.

He afterwards took up the study of the production of the methyl bases by heating together strong ammonia and methyl nitrate, as in the case of the ethyl bases. The chief product was methylamine. For the preparation of the methyl nitrate he found the use of urea, dissolved in the methyl alcohol, a most satisfactory modification. Subsequently he describes the separation of methylamine and its reactions, mentioning the salts methylamino-chloride of palladium and chloro-palladite of methylamine. In a later paper he describes triethylamine, its production, properties and reactions, and some of its salts.

In obtaining the urea for the preparation of the ethyl and methyl bases, Mr. Lea examined carefully the details of preparation of this substance from ferrocyanide of potassium, and by effecting a more complete oxidation by the use of a larger quantity of red lead he obtained as much as 500 grams of urea from 850 grams ferrocyanide.

In 1861, while preparing naphthylamine by the reduction of nitronaphthalin, he observed that if heat be applied before adding the caustic alkali a distillate is obtained which has a pale reddish color and which possesses the disgusting odor of naphthylamine. Mineral acids change its color to pale violet. Heated with sulphuric acid it becomes a rich blue-purple, and deposits after a time a small quantity of a black crystalline precipitate. Collected on a filter, this precipitate appeared in the form of nearly black needles with a most brilliant golden green glitter. On solution in alcohol, and evaporation, it was obtained as a dark red powder, which, when placed on glass and a platinum spatula drawn over it, gave a bright green, almost metallic reflecting surface, contrasting strongly with the red powder around it. The alcohol solution is of an intense dark blood red color, changing on the addition of a small quantity of sulphuric or nitric acid to an intense blue purple. For this new coloring matter he proposed the name *ionaphthine.*

Subsequently Carey Lea described another colored derivative of naphthalin, obtained in the course of preparation of the chloride by passing chlorine over it. On washing the crude product with ether and filtering, the ether, on evaporation, left a small quantity of a pale-yellow acid liquid, which after a time deposited a bright blue film, insoluble in water, alcohol, and ether. Exposed to ammonia gas, it became deep purple, the blue color being restored by acids.

In a paper published in 1865 he calls attention to a new reaction of gelatine, the first ever described as produced between pure gelatine and a perfectly colorless reagent. When a piece of gelatine is dropped into a solution of pernitrate of mercury it gradually assumes a strong red coloration and after a time dissolves completely to a fine red solution. On boiling for some minutes, its color deepens; but it is quickly decolorized by chlorate of potash. Metagelatine, prepared by allowing gelatine to swell in a cold saturated solution of oxalic acid, then heating moderately until the mass remained fluid on cooling, and removing the oxalic acid by carbonate of lime, was found to give the red coloration even more decidedly than ordinary gelatine.

In 1872 Mr. Lea published a criticism on a proposed method of estimating ethylic alcohol when present in methylic alcohol. The method is based on a determination of the melting point of methylic oxalate prepared from the methylic alcohol to be tested. If ethylic alcohol be present the melting point of the oxalate, which when pure is about 104° F., is claimed to be lowered. The author noticed that when well dried on blotting paper the crystals of methylic oxalate had precisely the same melting point, whether prepared from nearly pure methylic alcohol or from a specimen containing up to ten per cent. of ethylic alcohol. Evidently the crystals, when only squeezed, contain ethylic oxalate in the mother liquor, which of itself tends to lower the fusing point. The solidifying point observed experimentally would indicate the presence of only 3 or 4 per cent. of ethylic alcohol, whereas there was actually present in the sample 10 per cent. Evidently the method is not reliable.

In a paper on the detection of hydrocyanic acid Mr. Lea gives a new test for this substance. If a pure protosalt of iron, such as ferrous-ammonia sulphate, mixed with a little uranic nitrate, be dissolved in water, the solution gives, with a soluble cyanide, a purple precipitate, which in very dilute solutions is grayish purple. The solution should be quite neutral and nearly colorless. It is best made by mixing two solutions, each containing a grain or two of the respective salts in half an ounce of water. Two or three drops of the mixed solution are placed in a white porcelain capsule, and a drop or two of the liquid to be tested is allowed to trickle slowly down into it, noting the reaction at the point of contact. In this way the reaction obtained with a solution of potassic cyanide containing only one five-thousandth of a grain of hydrocyanic acid may be made to give a perfectly distinct reaction. As to the Prussian-blue reaction, the author points out that it is much more delicate than has been claimed, provided it be properly applied. If a weak ferrous solution containining a little ferric ammonia citrate be acidified with hydrochloric acid, and a few drops be placed in a white porcelain capsule, and a drop of the liquid to be tested be allowed to pass down the side of the capsule into it, a blue cloudiness will appear at the point of contact. In the author's experiments a distinct blue coloration appeared with a solution containing one grain of cyanide in four ounces of water, the drop containing, therefore, the equivalent $\frac{1}{5000}$ of a grain of hydrocyanic acid.

Besides his purely chemical papers, Carey Lea published many others in the domain of physics. As early as 1860 he called attention to the optical properties of picrate of manganese. This salt possesses markedly the remarkable property, pointed out by Brewster and Haidinger, of giving a colored ray by reflection, polarized perpendicularly to the incident plane, the color being quite different from that of the crystal itself. The picrate crystallizes in large and beautiful transparent right rhombic prisms, sometimes amber-yellow, sometimes aurora-red. Its optical properties are interesting, as it exhibits a beautiful dichroism. When viewed by light transmitted in the direction of its principal axis, it appears of a pale straw color; but in any other direction it is either a rich aurora-red in some specimens or a salmon color in others. Moreover, it possesses in a high degree the property of reflecting two oppositely polarized beams, which, since large crystals can easily be obtained, renders its examination easy. If a crystal be viewed by reflected light while it is held with its principal axis in the plane of incidence, the reflected light is not pure white, but shows a purple color. Examined with a dichroscope having its principal axis in the plane of incidence, the ordinary image is white, as usual, while the extraordinary one is purple. The crystals of picrate of manganese vary in color considerably. Those obtained by boiling picric acid with aqueous solution of cyanhydroferric acid and saturating with carbonate of manganese are of a deep rich color and show the purple polarized beam particularly well. This peculiar optical property should have a distinct name; and as the terms dichroism and pleochroism are used for transmitted light, the author proposes the term *catachroism* to express the property of reflecting two beams, one normally polarized in the plane of incidence and the other polarized in a plane perpendicular to it.

In 1861 Sprengel had devised an air blast for laboratory use founded on the well-known Catalan trompe (*Am. J. Sci.*, II, xxxii, 425). The following year Mr. Lea conceived that the principle might be made use of for aspirating as well as for blowing, and he described an apparatus performing both functions simultaneously, and admirably adapted to the purpose. This apparatus, in the form of the Bunsen filter pump, has since come into general use, especially for laboratory purposes; and, as modified and improved by Crookes, using mercury in place of water, it has made possible to science the high vacua which he has so thoroughly studied, and to electric lighting the construction of the incandescent lamp.

An ingenious paper by Mr. Lea was published in 1869 on certain phenomena of transmitted and diffused light. Having observed that when a beam of sunlight is thrown upon a white screen at fifteen or twenty feet distance, and a plate of finely ground glass is interposed, the white light acquires a deep orange-yellow color, he set himself to investigate the phenomenon. Three aspects of it were observed: First, where a strong beam of yellow, red, or reddish-yellow *direct* light is produced without the complementary blue being visible; second, where the yellow or red direct beam is visible and simultaneously the blue, the latter diffused; and, third, where reddish and bluish light, both diffused, are simultaneously visible. He concludes that all these results are due to interference and are capable of satisfactory explanation upon this hypothesis. To obtain the first result, take an ordinary plane silvered mirror, six by eight inches, and place it horizontally in a large beam of sunshine in a darkened room, so that the light is reflected to the wall or ceiling fifteen or twenty feet distant. Interpose, now, in the path of the ray after reflection, a plate of very finely ground glass. The ray which now passes through the colorless glass is no longer white, but deep yellow. As it is difficult to get glass finely enough ground, he suggests gelatinous alumina in a film of collodion or even copper hydrate in such a film, this latter arrangement showing the apparent paradox that colorless white light is dyed of a deep orange by passing through a bright blue film. The second result is obtained by the use of amorphous sulphur.

A few drops of sulphuric acid is added to fifteen or twenty ounces of water, and then two or three drops of ammonium sulphydrate. The sulphur, which separates in a few minutes, remains suspended in the liquid. Placed in a glass trough with parallel sides, a beam of sunlight sent through it and received on a screen fifteen or twenty feet distant is of a deep yellow color, while the liquid itself presents a rich blue tint. To obtain the third appearance, sago is made into a translucent paste with hot water largely diluted and placed in a flat gutta-percha dish, forming a layer at least an inch in depth. When an oblique beam of sunlight coming through a half-inch hole in the shutter falls upon the surface, it forms a bright oval surrounded by a halo two or three inches in diameter. The half of the halo farthest from the window is yellowish red, the other half bluish. To explain these phenomena the author considers one of the very small abrasions of the surface of ground glass. At its edge two parallel rays pass, one through the abrasion, the other through the original glass, the latter having traveled through a longer path in glass. If the index of refraction of the glass be 1.5, this ray will be retarded in the proportion of 1.5 to 1 for a distance equal to the depth of the abrasion. When this distance is extremely small, the blue rays will interfere. When large and of varying sizes, the various colors will produce white, as in the case of ordinary ground glass. If the abrasions are extremely small and very close, an excess of red light will be produced. Similar considerations apply to the second and third cases given above.

In 1896, shortly after the remarkable discovery of the Röntgen rays, Carey Lea made a series of very careful experiments to ascertain if these rays were detectable in sunlight. A very sensitive dry plate was placed in a book so that one hundred leaves and the red paper cover were between the sensitive film and the sunlight. A thick lead star was fastened to the outside of the cover and the whole exposed to bright sunshine for about seven hours. Not a trace of an image of the star appeared on development. Since Röntgen found his rays to penetrate one thousand printed pages, and moreover to traverse several meters of cardboard, the author's result is significant. A piece of sheet aluminum 1.2 millimeters thick was fitted into a frame, a very sensitive plate was placed behind it, and a lead star in front.

Not a trace of an image was obtained with three hours' exposure. Using a piece of white pine three-sixteenths of an inch thick, images were obtained by three minutes' exposure. On direct examination a panel of white pine one-fourth of an inch thick was observed to transmit red light. With full sunlight shining on thick card-board, a barium platinocyanide screen showed no indications of fluorescence. A thick disk of card-board, covered on one side with platinocyanide of barium, was placed in a tube which was directed to the sun. It showed fluorescence, but the interposition of very thin platinum foil cut off all the effect. Since Poincaré has expressed the opinion that all phosphorescent bodies emit Röntgen rays as well as light rays, the author exposed a dilute solution of uranin to sunlight, placing over it a sensitive plate protected by aluminum foil 0.1 millimeter thick, with a lead star interposed. An exposure of two hours gave no result. Repeated with quinine, five hours gave nothing. Rays from the Welsbach mantle, both with and without a chimney, were examined, but with no result. No rays capable of passing through aluminum foil 0.1 millimeter thick were detected by an exposure of five hours.

By far the most valuable as well as the most extended investigations of Carey Lea, however, were those which related to the chemistry of photography, in which at the time of his death he was the acknowledged authority. His researches were directed chiefly to the chemical and physical properties of the silver haloid salts, not only alone, but also in combination with each other and with various coloring matters, especially with reference to the action of light upon them under all these different conditions.

In one of Carey Lea's earlier papers, published in 1865, he gives a series of experiments which seem to him to decisively close the controversy then in progress in favor of the physical theory—*i. e.*, the theory that the change which takes place in an iodobromized plate in the camera is a purely physical one; that no chemical decomposition takes place, and hence that neither liberation of iodine nor reduction of silver results. In the first experiment he exposed and developed an iodobromized plate as usual, but instead of removing the unchanged iodide and bromide by fixing, he removed by means of a weak solution of acid mercuric nitrate the developed image without affecting the iodide and bromide. Obviously if the iodide or bromide had been in any way decomposed to aid in forming the developed negative image, there should have been left, on removing this, a more or less distinct positive image. Nothing of the sort was visible. The film was perfectly uniform, looking exactly as it did when it left the camera. In the second experiment the plate was treated similarly, except that the application of the mercuric nitrate was made in yellow light. It now showed nothing but a uniform yellow film; but, after washing, the application of an iron developer containing silver nitrate and citric acid produced the original image with all its details. As every trace of a picture as well as all reduced silver had been removed by the mercuric nitrate, it would seem to be absolutely demonstrated that the image is a purely physical one, and that after having served to produce one picture, that picture may be dissolved off and the same physical impression made to produce a second picture by a simple application of a developing agent.

In 1866 he prepared, by request, a résumé of a series of investigations whose object was to fix with greater exactness the obscure chemical and physical phenomena which lie at the basis of the photographic art, the details of which had been already published in the photographic journals. While it may be conceded that silver chloride and bromide undergo reduction while exposed to light, opinions differ as to the iodide, some holding that the action of light upon this haloid is purely physical; others that the change is an absolutely chemical one, reducing it either to a sub-iodide or even to metallic silver. In presence of free silver nitrate, reduction does in fact take place; but the important question now is, Does reduction of any sort invariably accompany the action of light upon silver iodide? Having produced specular films of pure metallic silver on plates of glass, iodizing them thoroughly, washing, exposing, and developing, and thus obtaining visible impressions, he conclusively proved that pure silver iodide is always sensitive to light. This established, he proceeded to the main question, Does chemical decomposition necessarily accompany the production of an impression upon silver iodide? In his view it does not. Pure silver iodide, he maintains, when exposed to light, receives a physical impression only; but if certain other substances, such as silver nitrate, tannin, etc., are present, then a chemical action, a reduction, may take place. In proof of the first statement a glass plate supporting a film of pure silver iodide was exposed to sunlight for many hours, then enclosed in a dark closet for thirty-six hours, then placed under a negative and exposed to light for two seconds. On pouring a developer over it a clear, bright picture instantly appeared. Hence the action of the sun for many hours had produced an impression which disappeared completely in thirty-six hours. Now, if the action of light is to reduce the iodide to sub-iodide, how did this sub-iodide recover its lost proportion of iodine? The fact that the iodide was much more powerfully affected by a recent exposure of two seconds than by one which, though thirty-six hours old, was many thousand times as strong, and in light much more intense, seems fatal to the chemical theory. By means of other direct and indirect experimental evidence he concludes that the action of light upon pure isolated silver iodide cannot be a chemical reduction: First, because the effect, even when carried many hundred thousand times further than in ordinary photographic processes, perfectly disappears in a few hours spontaneously, under circumstances which render it impossible to suppose that iodine could have been restored to replace that which must have been disengaged had any reduction taken place; second, because, even where the action of light is prolonged many hundred-thousand-fold the ordinary time, no reduced silver nor sub-iodide can be detected as present; third, because another metal, such as mercury, is capable of developing these images as well as silver; fourth, because a purely physical cause, to wit, mechanical pressure, is capable of producing a developable impression; and, finally, because there is not a single well-verified experiment which can be brought forward in support of the chemical view.

In a paper entitled "Contributions Toward a Theory of Photochemistry," published in 1867, Mr. Lea develops a remarkably ingenious theory based on the phenomena observed in silver iodide, which are the key to the whole subject. When this iodide is exposed to light it acquires a new property, that of attracting to itself a metallic precipitate in the act of forming, or a metallic vapor ready formed. A film of this iodide exposed for many hours to a bright sun does not further darken beyond the change produced by the first instants of diffuse light; and then if put aside in the dark for a brief time it re-acquires the capacity to receive an image by exposure for a second. What, then, is the nature of this change—this impression received in a second and then slowly passing spontaneously away? The answer Mr. Lea finds in the phenomena of phosphorescence. When silver chloride is exposed to light it becomes violet in color, losing one-half its chlorine—*i. e.*, it is decomposed; but when silver iodide is thus exposed no chemical change takes place, but the impression is for a time persistent. "The 'physical' impression of light is a persistence of the invisible (or 'chemical') rays exactly parallel to the persistence of visible or luminous rays in phosphorescence." In both cases the vibrations excited by light are not given out instantaneously, as in most light phenomena, where the return to photo-equilibrium is immediate, this equilibrium being reached only after an interval of hours or days. Evidently so long as these vibrations of non-luminous light continue, in the case of the iodide, for example, the body under their influence is much more disposed to suffer decomposition than when under normal influences; and if a film of such material has parts exposed to light, while other parts have been protected, and the whole be exposed to influences provocative of decomposition, it is evident that those influences may be so graduated that they will tell only upon the parts predisposed by the impression they have received. For this function of light, the existence of which produces the physical change suffered by exposed silver iodide, the author proposes the term *actinescence.* Just as in the case of phosphorescence, a body temporarily retains light and subsequently emits it, this emission being rendered evident by luminous phenomena, so by actinescence we have the phenomena described by Niepce de St. Victor as the storing up of light, where certain objects exposed to light and then carried into darkness have acquired the power of acting chemically upon other bodies with which they were placed in contact. Silver iodide when exposed to light in a state of perfect purity and isolated from all other substances undergoes no chemical change; carried into darkness it continues to vibrate in unison with the more highly refrangible rays, either those entirely beyond the visible spectrum or else those having a very low illuminating power, and this in so faint a degree that no phosphorescence is visible. If now it be brought into contact with any substance which would have occasioned decomposition in presence of light, then so long as this phosphorescence of actinic rays—this actinescence—continues' the same decomposition will take place. If simply left in the dark the actinescence will gradually expend itself precisely like ordinary phosphorescence. So, in both cases, a fresh exposure to light will create a fresh impression, the impressed material having perfectly recovered its original condition. "This theory," he says, "rests upon two properties for whose existence I have long contended, and which I believe I have succeeded in establishing, namely, the sensitiveness to light of iodide of silver even when perfectly isolated, and its spontaneous recovery of that sensitiveness after obliteration through powerful action of light, by simply remaining in darkness." He therefore concludes "that the latent image is simply due to a phosphorescence of chemical or actinic rays, to which property I give the name of *actinescence.*

In a paper read before the American Association for the Advancement of Science at Newport in 1868, Mr. Lea pointed out the well-known fact that silver bromide, when exposed to light, undergoes decomposition, with elimination either of bromine or a bromine compound, being at the same time reduced to subbromide, the result being a distinct darkening. In his experiments organic matter was eliminated by forming the film on a plate of glass, first by silvering it and then treating it with bromine or iodine. On exposure for four hours the pure and isolated bromide film gave a distinct impression. Since silver iodide is not thus decomposed, the latent image produced by its exposure to light must be purely physical. The object of the paper was to show that silver bromide is also capable of forming a latent image, in which chemical decomposition plays no part, and which therefore must be considered as a mere molecular alteration, a physical as distinguished from a chemical image. This physical image, however, is quite different from that formed on silver iodide. While on the latter the physical image is produced only when the iodide is isolated from all other bodies, that on the bromide is found only in the presence of organic matter; and, secondly, while the physical image on silver iodide can be called forth only in the presence of silver or of some other metallic body, this image on silver bromide can be developed in the complete absence of any metallic body. Let a collodion film containing silver bromide and free silver nitrate be formed on glass, washed, plunged into a solution of tannin, and dried. Expose this for a short time in the camera. A latent image is formed. Place the plate in pyrogallol solution and the image appears. But how is this? It cannot be that an infinitesimal chemical image of sub-bromide, acting as a nucleus, was brought up to a visible intensity by the action of the developer, because pyrogallol alone has no power to do this, and because free silver nitrate must also be present, and this had been removed in the washing. The only alternative is that that portion of the film upon which the light had acted was so modified thereby that it was brought into a condition to be more easily decomposed by pyrogallol than the portion which had not been acted on. Now, if portions of the bromide film not decomposed by light, but simply acted on by it, are subsequently decomposed by the action of pyrogallol, while those portions of the film not influenced by light are not decomposed by the pyrogallol, then it follows that the action of the light is so far simply physical.

In 1878 Carey Lea sought to determine the precise amount of material actually altered by the action of light. Silver chloride, precipitated with excess of hydrochloric acid, and well washed, was exposed to bright sunlight for five days. Two grams of the dark powder were thoroughly treated with sodium hyposulphite to remove the unaltered chloride. The residue weighed twenty-one milligrams, showing that only about 1 per cent. of the chloride had been acted on. If we suppose the action to consist in the removal of one-half the chlorine, the whole loss in weight by the action of the light would be only a little more than one-tenth of 1 per cent. As the best reagents for removing the unaltered chloride are liquid ammonia and sodium hyposulphite, and as both of them attack the altered substance, the difficulty in verifying the nature of the action of light is very considerable. Nitric acid does not attack the darkened portion of the silver chloride in the least, while the dark residue left by the above reagents is instantly dissolved by cold nitric acid with evolution of red fumes. Evidently no metallic silver is produced by the action of the light, while it is produced by the subsequent action of the ammonia and the hyposulphite. Since the black substance is made white by *aqua regia*, it evidently contains less chlorine than the chloride, and so may be either a subchloride or an oxychloride.* The substance produced by the action of light on silver chloride is of a much more permanent character than in the case of the other silver haloids.

When silver iodide is blackened under ammonia solution in a test-tube and set aside in the dark for a day or two, the iodide assumes a singular pinkish shade. Hence it appears that silver iodide, under the influence of ammonia and of light, gives indications of most of the colors of the spectrum. Starting with white, it passes under the influence of light to violet and thence nearly to black. This violet-black substance, washed with water, passes to brown. The brown body, covered with ammonia and left to itself in an open test-tube, becomes pinkish in the dark, yellow in sunlight. These curious relations to color which we see in the silver haloids seem to give hope of the eventual discovery of some complete method of heliochromy.

In 1874 Carey Lea made an extended series of experiments to test a theory advanced shortly before by Dr. Hermann Vogel, to the effect that substances placed in contact with silver bromide modify its impressibility by rays of different refrangibilities. Moreover, he maintained that the change will follow a certain law—*i. e.*, that colored substances absorbing certain rays will increase the impressibility of the bromide to those rays which they absorb. Thus a colored substance which absorbs the yellow rays and radiates the rest of the spectrum will increase the sensitiveness of silver bromide to the yellow ray. Mr. Lea's results seemed to establish the fact that there is no general law connecting the color of a substance with the greater or less sensitiveness which it brings to any silver haloid for any particular ray.

The following year Mr. Lea made an elaborate investigation on the action of the less refrangible rays of light on silver iodide and bromide. The effects upon the silver compounds were obtained by forming them in the body of pure paper, the silver solution being applied in all cases after that of the alkali-haloid, and the paper thoroughly washed. Colored glasses were used to obtain the colored light, in preference to the spectrum itself, the absorption spectrum of these glasses being exactly determined

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* Proved later to be a subchloride.

with the spectroscope. Experiments were also made to test the theory of E. Becquerel, according to which light consists of two classes of rays, the "exciting" and the "continuing" rays. The more refrangible rays alone have the power of originating an impression; the less refrangible were powerless to commence, but were capable of continuing and reinforcing an impression which had been commenced by the more refrangible rays. The conclusions reached by the author as a consequence of the one hundred and sixty experiments made were:

1. Silver bromide and iodide are sensitive to all the visible rays of the spectrum.
2. Silver iodide is more sensitive than the bromide to all the less refrangible rays, and also to white light.
3. The sensitiveness of silver bromide to the green rays is materially increased by the presence of free silver nitrate.
4. Silver bromide and silver iodide together are more sensitive to both the green and the red rays (and probably to all rays) than either the bromide or the iodide separately.
5. There do not exist any rays with a special exciting or a special continuing power, but all the colored rays are capable both of commencing and continuing the impression on silver iodide and bromide.

In a research published in 1876 Mr. Lea confined himself to the question: Does there exist any red substance which is capable of increasing the sensitiveness of silver bromide to the green rays? Of all the red pigments tested, corallin was the only one which produced the slightest increase of sensitiveness to the green rays. But for two good reasons this power cannot be considered as a function of its color: First, because it shows a still more marked tendency to increase the sensitiveness of silver bromide to the red ray than to the green; and, second, because it is easy to destroy its action on green light without destroying its color. Moreover, he observed that many entirely colorless substances gave an increase of sensitiveness to the green rays. So that it is not among the colored but among the colorless substances that we must look for those capable of enhancing sensitiveness to green light. Not a single red substance could be found that possessed that property, while no less than eight colorless substances exhibited it. The conclusion is the same as before: "There exists no relation between the color of a substance and that of the rays to which it increases the sensitiveness of silver bromide."

In 1877 Carey Lea pointed out that salts of silver may exhibit sensitiveness to light in three ways: They may exhibit a sensible darkening or they may receive a latent image; and this image may have a capacity of being rendered visible either by receiving a deposit of metallic silver or by decomposition by alkalies in connection with reducing agents. The last two phenomena are quite distinct, since in the first the image is produced entirely by the addition of silver not previously present, while in the second no silver whatever is added, that portion of substance which received the direct action of light undergoing decomposition by subsequent treatment. The action of light sets up a molecular change in both cases. In the one case the portions acted on by light become more apt to attract a precipitate in the act of formation; in the other they are more readily attacked by certain reducing agents. Of course the silver compounds which show the greatest tendency to form latent images by the action of light are the chloride, bromide, and iodide; but the same tendency exists, though in a less degree, in other compounds, as was shown many years ago by Robert Hunt, in the case of other silver salts. Out of twenty-four silver salts examined, the author found eleven which gave latent images capable of development by the action of pyrogallol and ammonia. Curiously enough, it was observed that no substance insensitive in the absence of tannin acquired sensitiveness by its presence.

Since the development of the latent or invisible photographic image produced by the action of light is, beyond all question, the most remarkable and the most interesting fact in photochemistry, it is surprising with what slowness our knowledge of the substances capable of producing this effect has increased. In 1877 Carey Lea made an extended examination of substances likely to act as developers. Since in general the effect is a reducing one, it is among reducing agents that these substances are likely to be found; but not only this—an elective power is needed; a tendency to reduce, not the whole surface, but only those parts that have been acted on by light, and to spare the others. The results show (1) that the number of bodies endowed with the power of developing the latent image, so far from being very limited, as hitherto supposed, is, on the contrary, very large; and (2) that potash acts more powerfully in aiding development than ammonia, contrary to the general opinion. Moreover, he observed that the use of free alkali is not necessary to the most energetic development, as has been supposed; and this led him to devise a form of development which, though there is no free alkali present, is more powerful than any yet known. He also disproved the common impression that ferrous salts act only in presence of a soluble salt of silver, and in its absence scarcely attack the silver haloid in the film to produce the image. Among the various developing substances examined, the salts of ferrous oxide proved to be the most interesting and remarkable of all in their action on the image; and of these, ferrous oxalate exhibits developing powers of a very marked kind. The same exposure which with alkaline pyrogallol gives a weak and sunk-in image after a protracted development gives with ferrous oxalate a bright, bold image and in much less time. The development is particularly clear and clean. The unexposed parts are not attacked. The developer possesses a great deal of that elective power previously mentioned, which causes it to react strongly on those parts which have received the influence of light, and to spare those which have not. Three years later the study of the developing power of ferrous salts was resumed and extended to include many inorganic compounds. The most active ferrous salts found were the borate, phosphate, sulphite, and oxalate.

The fact is well known that certain organic substances, tannin, for example, placed in contact with the washed haloid, increase its sensitiveness. Poitevin and Vogel proposed the theory that these substances acted in virtue of their affinity for the halogen. But Carey Lea pointed out soon afterward that the one property that these substances possess in common is that they are all reducing agents. Hence he concludes that their action is due to the fact not that they abstract the halogen, but that their affinity comes in to aid the affinity of the halogen for the hydrogen, and that under the influence of the light water is decomposed. According to this view, whenever silver iodide is exposed to light in presence of an organic body capable of accelerating the action of this agent, there should be formed traces of free acid; whereas the Poitevin-Vogel theory requires the formation of an iodo-substitution compound. To test the question, silver iodide precipitated with excess of potassium iodide and well washed, was exposed, after receiving a small quantity of pyrogallol, to sunlight for fifteen minutes in presence of water. The liquid, which was at first neutral, showed a distinct acid reaction at the end of fifteen minutes. Again, on the Poitevin-Vogel theory, substances having an affinity for iodine should increase the sensitiveness, and substances not having it should have no such action. But this is not the fact. Substances like potassium carbonate solution and like starch, for example, which have an affinity for iodine, do not appear to increase the sensitiveness of silver iodide by contact with it. Hence he concludes that such organic bodies as increase the sensitiveness of the silver haloids to light do so not by forming substitution compounds with the halogen, but by promoting, in virtue of their affinity for oxygen, the decomposition of water by this halogen.

As early as 1866 Carey Lea had proved that the intense black substance produced by the action of light upon silver iodide in presence of silver nitrate contains iodine, and therefore is either a sub-iodide or an oxy-iodide. In 1874 he extended his examination to silver bromide. He observed that when silver bromide is treated with pyrogallol and alkali after exposure to light, the black substance contains bromine, and is resolved by nitric acid into normal silver bromide and silver, which latter is dissolved. It is therefore either a sub-bromide or an oxy-bromide, probably the former. In 1878 he proved the same fact for the black substance given by the chloride when acted on by light.

Perhaps the most important contribution made by Carey Lea to photochemistry was his discovery of what he termed photosalts. His earliest paper on the subject appeared in 1885, and described the remarkable property possessed by the silver haloids of entering into chemical combination with certain coloring matters in somewhat the same way as alumina does, forming lakes. The freshly precipitated and still moist silver salt is brought into contact with the coloring matter, or it is precipitated in presence of it. The union takes place readily, and the color cannot be washed out. What is curious and seems to be evidence that the combination is intimate is the fact that the color assumed by the silver salt may differ considerably from that of the dye. The three haloids may even be differently colored by the same coloring substance. Generally, however, coloring matters impart their own shade or something like it to the haloid. The bromide precipitated in presence of silver nitrate takes from aniline purple a strong purple color, from cardinal red a bright flesh or salmon color, from naphthalin yellow a yellow color. Sometimes different specimens of the same coloring matter give different colors. Silver bromide received from one specimen of methyl green a bluish green, while another specimen of the same dye produced in it a deep purplish color. Already in 1868 he had proposed* to color or stain the photographic film in order to modify its behavior toward light—*i. e.*, to prevent blurring or irradiation. At that time the best color was found to be red litmus. The theory of Vogel that a film thus colored gained sensitiveness to those rays of the spectrum which the coloring matter absorbs is made improbable by the fact that the color in the film tends to arrest precisely those rays to which it is proposed to render the silver salt more sensitive. John W. Draper's view that substances sensitive to light are affected by the rays which they absorb seems *a priori* more probable. The author, however, observes that the effect will depend, first, upon the capacity of the dye to combine with the silver haloid, and, second, not on the proper color of the isolated dye, but on the color that the silver haloid acquires from it.

The paper containing his photosalt theory was published in 1887. Of the two theories of the latent photographic image, the physical and the chemical one, he had inclined at the outset to the first of these. Of late years results had been obtained not readily reconcilable with it. On the other hand, the theory that the latent image is formed of subsalts is open to the objection that while subsalts are readily attacked by nitric acid, the latent image may be exposed without effect to this acid. Three years of laboratory work had led him to a truer theory, based on the fact that the silver haloids are capable of uniting with coloring matters to form stable compounds. He now finds that in much the same way a silver haloid may unite with a certain proportion of its own subsalt to form colored compounds, which by this union quite loses its characteristic instability and yields a compound of great permanence. When now silver chloride,

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* British Journal of Photography, xv, 210, 506, 1868.

bromide, or iodide contains as little as one-half of one per cent. of subsalt combined with it, its properties are greatly changed. It has a strong coloration and its behavior to light is altered. It is one of the forms of this substance which constitutes the actual material of the latent photographic image. Of the three, the chlorine salt is the most stable and exhibits the finer variety of coloration. Hence it is the most interesting because of its relations to heliochromy. It shows all the warm shades from white to black through the following gradations: white, pale flesh color, pale pink, rose color, copper color, red purple, dark chocolate black. These compounds are obtained in an endless variety of ways—by chlorizing metallic silver; by acting on normal chloride with reducing agents; by partly reducing silver oxide or silver carbonate by heat and treating with hydrochloric acid, followed by nitric acid; by acting on subchloride with nitric acid or an alkaline hypochlorite; by attacking almost any soluble salt of silver with ferrous, manganous, or chromous oxide, followed by hydrochloric acid; by reducing silver citrate by hydrogen and treating it with acid; by treating a soluble silver salt or almost any silver solution with potash or soda and almost any reducing agent—cane sugar, milk sugar, glucose, dextrine, aldehyde, alcohol, etc.—and supersaturating it with hydrochloric acid. So, also, almost any salt of silver exposed to light, treated with hydrochloric acid and then with strong nitric acid yields it. Since these substances have been seen hitherto only in the impure form in which they are produced by the continued action of light on the normal salts, the author proposes to call them *photosalts;* as *photochloride*, *photobromide*, and *photoiodide.*

In the second part of his paper the author gives evidence to prove that the strongly colored photosalts now described, obtained independently of any action of light, are identical, first, with the product obtained by the continued action of light on these haloids, and, second, with the substance of the latent image itself. If silver chloride precipitated with excess of hydrochloric acid be exposed to light, we get a deep, purple-black substance which, when boiled with dilute nitric acid, gives up a little silver and becomes a little lighter, changing to a dull purple, resembling closely some of the forms of photochloride already described, chiefly those produced by the action of sodium hypochlorite or of ferric chloride on metallic silver. When silver oxalate is covered with water and exposed to sunshine for two days, being frequently agitated, it changes to a deep brownish black, becoming a little lighter by treatment with hydrochloric acid. When washed and boiled with nitric acid it acquires a fine deep copper-red color. A sample especially prepared in this way which had a fine lilac purple color was found to contain one-half of 1 per cent. of subchloride. The red chloride thus obtained by the action of light on silver oxalate not only resembles closely the red chloride obtained by means exclusively chemical, but shows the same behavior to reagents. Other silver salts were examined, and it was found that all of them thus treated yielded pink or red photochloride. In considering the question of the latent image the author calls attention to the remarkable fact that a dilute solution of sodium hypophosphite if poured over a mass of silver chloride, bromide, or iodide formed in the absence of light, produces no visible effect, but has the property of bringing those substances into the condition in which they exist in the latent image. Applied in strong solution with the aid of heat it produces brown photochloride, photobromide, or photoiodide of silver. Experimental evidence is given to show, first, that in the entire absence of light sodium hypophosphite is able to affect a sensitive film of silver haloid exactly in the same way as does light, producing a result equivalent to a latent image formed by light and capable of development in the same way as an actual impression of light; second, that these two effects, the impression produced by hypophosphite and that by light, comport themselves to reagents exactly in the same way, and seem in every way identical; and, third, that the image produced by hypophosphite on silver chloride always gives rise to a positive development, but on silver bromide may give rise either to a direct or to a reverse image, both of these effects corresponding exactly with those of light. But more than this. Sodium hypophosphite may be made to reverse the image produced by light on silver bromide and, conversely, light may be made to reverse the action of hypophosphite. It would seem, therefore, that the question of the identity of the photosalts with the products of light on the silver haloids may, perhaps, with some confidence be allowed to rest on the cumulative proofs here offered.

In connection with the papers just referred to, Mr. Lea published soon afterwards a suggestive communication on what he calls "Image Transference." He had already shown that it was possible to make marks with sodium hypophosphite upon a silver haloid film, and then to obtain a development of these marks precisely as if they had been impressed by light, but of course quite independent of any exposure thereto. He now proves that it is possible to develop on a film of silver haloid a complete image—a print from a negative, for example—without exposing the silver haloid either to light or to the action of hypophosphite or subjecting it to any treatment whatever between the moment of its formation and that of its development. The film of silver comes into existence with the image already impressed upon it. A film of silver salt, citrate, benzoate, tartrate, pyrophosphate, etc., is formed on paper in the ordinary way, and this is exposed, under a negative, to sunshine for a few seconds. Then by plunging the film into dilute hydrochloric or hydrobromic acid it is converted into silver chloride or bromide. The acid is then washed out; and now, on putting the film, thus converted into silver haloid, into a ferro-oxalate developer, the image appears at once. The silver chloride or bromide comes into existence with the image already impressed upon it at the instant of its formation; so that, although the substance which received the image is completely broken up and destroyed, the image is not, but is transferred in all its details to the new film of silver haloid. It is therefore evident that the action of light on all silver salts that can thus transfer an image must be similar in all its essentials to the action of light on the silver haloids. Hence it follows that all such silver salts must be capable of forming subsalts, else the image could not be transferred.

In further support of his position that the principal and characteristic product of the action of light on the silver haloids is a combination of the haloid with a small proportion of its own subsalt, the author in 1887 offered direct evidence of the fact that silver chloride can unite with small quantities of other metallic chlorides. "That an actual combination, though one quite outside of atomic proportion, takes place, is proved by two facts: first, that the chloride with which the silver haloid unites, though soluble in water, is not removable by water; and, again, that the properties of the haloid are markedly changed." Thus if ferric chloride is added to dilute hydrochloric acid, and then silver nitrate, the silver chloride precipitated is not white, but buff colored. The ferric chloride cannot be removed by washing, and even hydrochloric acid removes it only in part; but even this minute quantity of iron profoundly affects the sensitiveness of the silver salt to light. In a comparative test the normal silver chloride had passed to a full violet with an exposure which produced on the other scarcely any visible effect. Similar results were obtained with cobalt, nickel, and manganese.

As long ago as 1878 Mr. Lea had pointed out that as the black substance produced by the action of light upon silver chloride became white on treating it with *aqua regia*, it evidently contained less chlorine than the chloride, and so must be either a subchloride or an oxychloride. Subsequent investigations immensely strengthened the presumption that it was a subchloride, especially the remarkable discovery of photosalts and their rôle in photography. Since, however, advocates of the oxychloride theory still existed in 1889, the author undertook to settle the question by what he calls proof by exclusion. Silver chloride was precipitated with excess of hydrochloric acid, washed in a darkened room, and dried in a desiccator. It was then placed in a porcelain crucible, fused, and poured into naphtha in a vessel carefully freed from moisture. The chloride solidified to a pale-gray lump, which, while in the naphtha, was absolutely free from all possibility of contact with oxygen. On moving the vessel into the sunshine the chloride instantly became as black as ink. In a second experiment the converse method was used. Pure silver, reduced by cadmium from the chloride, was heated nearly to redness in a porcelain capsule and dropped into naphtha. Some fragments of iodine were added. The action, though slow, was continuous and regular. After some hours the whole of the iodine had united with the silver to form a black compound. It is clear, therefore, that, whether we start from silver chloride and proceed by reduction, or from metallic silver and proceed by iodization, we can, in either case, obtain a photosalt under conditions which rigorously exclude all possibility of the presence of oxygen or of moisture in any shape. The photosalt, therefore, is not an oxysalt, but a compound of normal salt with subsalt.

In further proof of the existence of hemi-compounds—*i. e.*, of compounds intermediate between the normal salts and the metal, such as the hemihaloids of silver, which play so important a part in the photosalts—Mr. Lea published, in 1892, a paper on silver hemisulphate, which he had obtained as a double salt of hemisulphate and normal sulphate containing one molecule of each. The new salt has a bright brown color and has a stability which, in view of its composition, is remarkable. Nitric acid, unless very strong, has but little action on it. Ferrous sulphate, which instantly reduces silver sulphate, has no action on it whatever. Hot sulphuric acid is without action. The new substance was formed by the joint action of sulphuric and hypophosphorous acid on a silver salt, the silver sulphate being formed in presence of the hypophosphorous acid. Either the nitrate, phosphate, or carbonate may be used.

Perhaps the most remarkable discovery made by Carey Lea is that of allotropic silver. Early in the year 1886 he had taken up the study of the reduction products of silver in connection with that of the photosalts. At first the results were most enigmatical, but eventually stable products, capable of a fair amount of purification, were obtained. The reaction employed was the reduction of silver citrate by ferrous citrate. Even the earlier and less pure forms of allotropic silver thus prepared were exceedingly beautiful; the purer are hardly surpassed in this respect by any known chemical products. The forms obtained he classifies as: A, soluble, deep red in solution, mat-lilac, blue, or green while moist, brilliant bluish green, metallic when dry; B, insoluble, derived from A, dark reddish brown while moist, when dry somewhat resembling A; C, gold silver, dark bronze while wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-colored. The C form is insoluble in water and appears to have no corresponding soluble form. All these forms have several remarkable properties in common. These are: (1) that of drying with their particles in optical contact, and consequently forming a continuous film; C, when so treated, would be taken for gold-leaf; on glass, an absolutely perfect mirror is obtained; (2) that of taking a very beautiful coloration when brushed over paper and exposed to the action of any haloid solution; with sodium hypochlorite the results are often magnificent, giving intense shades, with metallic reflections, reminding one of the colors of a peacock's tail; (3) that of being converted by the stronger acids, even when much diluted, into normal gray silver—a change which takes place absolutely without any separation of gas; and (4) that of being easily reduced to an impalpable powder. To see what is apparently solid burnished metal break easily in pieces and yield a fine powder by moderate trituration is surprising. In preparing the A form of allotropic silver, concentrated solutions of ferrous citrate and a silver salt are mixed together. The liquid turns almost completely black and deposits in 10 or 15 minutes a heavy precipitate of a fine lilac-blue color. When thrown on a filter it takes a deep blue color, without losing its solubility. In water it dissolves with an intense blood-red color, but it is insoluble in a 5 or 10 per cent. solution of sodium nitrate, citrate, or sulphate, or of ammonium nitrate. After several re-precipitations and washings, first with ammonium nitrate and then with alcohol, and drying, three analyses gave 97.31, 97.18, and 97.21 per cent. of silver, the other 2 or 3 per cent. being shown to be ferric oxide and citric acid as an accidental impurity. The inference seems to be very strong, therefore, that there exists an allotropic form of silver freely soluble in water. From this solution it is readily precipitated by the addition of almost any neutral substance, in either a soluble or an insoluble form. Alkali sulphates, nitrates, and citrates throw down the soluble form; magnesium, copper, ferrous and nickel sulphates, and even silver nitrate, throw down a perfectly insoluble form of a purple-brown color. This insoluble form may be made to return to the soluble condition by a dilute solution of sodium borate, which gives a brown solution; by one of sodium sulphate, which gives a yellowish red one, and by one of ammonium sulphate, also a red one. The insoluble variety is soluble in ammonia, giving a fine red solution. The gold yellow and copper-colored silver is obtained by mixing solutions of silver nitrate, ferrous sulphate, and Rochelle salt in definite proportions. A powder, at first glittering red, then changing to black, is thrown down, which on the filter becomes of a beautiful bronze color. It is spread on a watch glass and allowed to dry. It forms lumps exactly resembling highly polished gold. On analysis it gave 98.75 per cent. silver. Experiment showed the density of allotropic silver to be less than that of normal silver, the blue substance, B, giving 9.58, the yellow variety, C, 8.51, that of normal silver being about 10.5. Moist gold-colored silver is converted into normal silver by the action of light. As thus produced, it is exquisitely beautiful, having a pure and perfect white color, like the finest frosted jeweler's silver. All the forms of allotropic silver are sensitive to light. Their stability is very variable, and this under conditions so far difficult to define.

Mr. Lea subsequently points out that the three forms of allotropic silver above mentioned are not to be understood as the only forms which exist, but only as the most marked. The substance is protean. No other metal appears to be capable of assuming such a remarkable variety of appearances. Metallic silver has been obtained—blue, green (many shades of both), red, yellow, and purple. An intense yellow-brown solution of allotropic silver was changed by a little solution of disodium phosphate to bright scarlet, presently decolorizing with formation of a purple precipitate, which in its turn, when washed on a filter, changed to bluish green.

In his paper of March, 1891, Mr. Lea undertakes (1) to describe the reactions of gold-colored allotropic silver; (2) to show that a well characterized form of silver exists intermediate between the allotropic silver already described and ordinary silver, differing in a marked way from both; (3) to prove that all the forms of energy act upon allotropic silver, converting it either into ordinary silver or into the intermediate form; mechanical force and high-tension electricity converting it directly into ordinary silver, while heat and chemical action convert it, first, into the intermediate form, then into ordinary silver; light produces the intermediate form only; and (4) to show that there exists a remarkable parallelism between the action of these forms of force on allotropic silver and their action on the silver haloids, indicating that it is not improbable that in these haloids silver may exist in the allotropic condition. As to the intermediate form, he finds that if a chemically clean glass plate be coated with a film of gold-colored allotropic silver, allowed to dry, first in the air and then at 100° C. for an hour or two, and then, if the middle of the plate be carefully heated over a spirit lamp, there is obtained a whitish-gray circle with a bright, lustrous, golden-yellow ring about it, somewhat lighter and brighter than the portion of the plate that has not been changed by heat. This ring consists of what he proposes to call the "intermediate form." Its properties are better seen by using a film formed on pure paper, one end of which is heated over a spirit lamp to a temperature just below that at which paper scorches. The change is sudden and passes over the heated portion of the surface like a flash. On examining the changed part we find: First, that it has changed from a deep-gold to a bright-yellow gold color; second, that it does not whiten or change color in the slightest degree when subjected to a shearing stress; third, that it is much harder, as is readily perceived on burnishing it; and, fourth, that it no longer shows the color reaction with potassium ferricyanide and ferric chloride, changing only by a slight deepening of color. This paper concludes with an interesting résumé of the action of different forms of energy on allotropic silver, and discusses its color reactions with the aid of beautifully colored lithographic plates.

In his paper of April, 1891, Mr. Lea sums up his conclusions as follows: "That silver may exist in three forms: First, allotropic silver, which is protean in its nature; may be soluble or insoluble in water, may be yellow, red, blue, or green, or may have almost any color, but in all its insoluble varieties always exhibits plasticity—that is, if brushed in a pasty state upon a smooth surface its particles dry in optical contact and with a brilliant metallic luster; it is chemically active; second, the intermediate form, which may be yellow or green, always shows metallic luster, but is never plastic and is almost as indifferent chemically as white silver; third, ordinary silver." Further he points out "that allotropic silver can always be converted either into the intermediate form or directly into ordinary silver; that the intermediate form can always be converted into ordinary silver, but that these processes can never be reversed; so that to pass from ordinary silver to allotropic it must first be rendered atomic by combination, and then be brought back to the metallic form under conditions which check the atoms in uniting; that allotropic silver is affected by all forms of energy, and that this effect is always in one direction, namely, toward condensation; that the silver haloids are similarly affected by the same agencies; that a remarkable parallelism is noticeable between the two actions, especially if we take into account the fact that in the haloids the influence of energy is to some extent restrained by the strong affinity which the halogens show for atomic silver. There is therefore reasonable ground to suppose that in the silver haloids silver may exist in the allotropic form.

In the course of his investigations Mr. Lea had become greatly interested in the relations of energy to the chemical changes in matter. Since it is well known that when a substance is capable of existing in two allotropic forms and of being converted from one into the other by pressure, the body resulting from pressure is always the more dense of the two, is less active chemically, and is a polymer of the first, it should follow that allotropic silver, which is converted into normal silver by the simple pressure of the finger, should be less dense than it and should have a greater chemical activity. This Mr. Lea has shown to be the fact. In the case of the three forms of silver—the allotropic, the intermediate, and the ordinary form—he pointed out as early as 1891 that while the first form can be converted into the second and third in several ways and with the utmost facility, and that the second can also be converted into the third, these transformations can by no possibility be reversed. To convert ordinary into allotropic silver we must as a first step dissolve it in an acid—that is, convert it from a polymerized into an atomic form—since only from this atomic form can allotropic silver be obtained. Hence he suggests that the three forms of silver may be considered as atomic, molecular, and polymerized. Special experiments made upon the silver haloids showed that these compounds, though substances of very great stability, have their equilibrium so balanced as to respond to the slightest influence, not merely of light, but of any form of energy; not receiving a momentary but a permanent impression, which, though so slight as to be invisible, still greatly increases the tendency of the molecule to fall in pieces under the action of a reducing agent. It is not light only, therefore, that is capable of producing an invisible image. The power belongs alike to all forms of energy. In his paper read before the National Academy in April, 1892, he showed that not only heat, light, electricity, and chemism are capable of disrupting the molecule, but that mechanical force also is able to do this. Silver chloride was enclosed in platinum foil and exposed to a pressure of about one hundred thousand pounds to the square inch, maintained for twenty-four hours. The chloride was completely blackened except at its edges, where, of course, the pressure was less. Silver bromide gave the same result. Silver iodide is not blackened by light; but, to his great surprise, it darkened under pressure to the same extent as the others. Even shearing stress obtained by simple trituration in a porcelain mortar produced a darkening of silver chloride—a true silver photochloride. These observations prove the existence of a perfect uniformity in the action of all kinds of energy on the silver haloids. The balance of the molecule is at once affected by the influence of any form of energy. A slight application produces an effect which, though invisible to the eye, is instantly made evident by the application of a reducing agent. The bonds which unite the atoms have evidently been loosened in some way, so that these molecules break up more easily than those to which energy has not been applied. Hence, if the substance be submitted to the action of light, heat, or electricity, or if lines are drawn across it with a glass rod or with sulphuric acid, a reducing agent blackens the parts so treated before it affects the parts not so treated. Obviously the phenomena of the latent image and of its development are not especially connected with light, but belong to other forms of energy as well. It follows, therefore, that every form of energy is capable, not only of producing an invisible image—that is, of loosening the bonds which unite the atoms—but also, if applied more strongly, of totally disrupting the molecule. Mechanical force, even, is therefore competent without the aid of heat to break up a molecule which owes its existence to an exothermic reaction. Obviously this phenomenon has nothing in common with decompositions produced by mechanical force in silver or mercury fulminate and similar explosives. Such substances are all formed by endothermic reactions, and their decompositions are exothermic. But silver haloids are formed by exothermic reactions, and consequently their decompositions are endothermic and require the energy which was set free in their formation to be returned to effect their decomposition. The experiments now described show that mechanical force may be made to supply this energy, and so play the part of light, electricity, or heat without previous conversion into any of these forms.

In a paper on " Endothermic Reactions Effected by Mechanical Force," published in 1893, Mr. Lea generalized his proposition and sought to determine whether the same agent—*i. e.*, mechanical force—would not be capable of bringing about analogous chemical changes in other compounds. By means of a powerful press the following reactions, all endothermic, were produced: Silver sulphite, salicylate and carbonate, ammonium platinochloride, and mercuric oxychloride underwent a well-marked darkening. Since these reactions are endothermic, it follows that mechanical force can bring about reactions which require an absorption of energy, which energy is supplied by the mechanical force precisely as light, heat, and electricity supply energy in the endothermic changes which they bring about.

In the second part of this paper Carey Lea not only adds to the number of endothermic reactions produced by mechanical force, but in one case has been able to obtain actual quantitative results, the mechanical force being applied in the form of shearing stress produced by sharply grinding the material in a mortar. Thus mercuric chloride, which did not darken in the least with ammonia, became gray very readily after fifteen minutes' trituration. Mercurous chloride became at first yellow and then blackened without difficulty. Mercuric iodide and oxide, platinic chloride, silver tartrate, citrate, and oxalate all blackened. Half a gram of sodium chloraurate gave in half an hour 10.5 mgrms. of gold. Calculation shows that the amount of energy absorbed in setting free the 10.5 mgrms. of gold would raise 518 grams to the height of one meter. Hence 518 gram-meters represent the amount of mechanical energy transformed into chemical energy in this experiment. The production of endothermic change by shearing stress can be very simply shown by soaking strong paper in a solution of the substance, very thoroughly drying it, then laying it upon a plate of glass and rubbing it strongly with the end of a glass rod.

In a third paper on this subject Mr. Lea gives additional examples of the transformation of mechanical into chemical energy. In one case half a gram of mercuric oxide was triturated in a porcelain mortar, and 30.5 mgrms. of mercury were obtained. Calculating the energy required to reduce this quantity of mercuric oxide to mercurous, it corresponds to 322 gram-meters, which is the amount of mechanical energy transformed into chemical energy.

In 1895 and 1896 Carey Lea published two ingenious papers on the Color Relations of Atoms, Ions, and Molecules. In the first of these, read before the National Academy in April, he points out (1) that the atoms of which elements are composed differ remarkably in color from the elements themselves, and (2) that their colors are more important and more characteristic than those of the elements. So that if we divide the entire series of elements into two classes, (*a*) those whose atoms are always colorless, whatever may be their valency, and (*b*) those whose atoms are either sometimes or always colored, we shall find that this division harmonizes in a striking way with their chemical properties. The fact is remarkable that it is never possible to deduce the color of an atom from that of the element which it forms by combining with another similar atom. Between the atom and the element there seems to be no color relation whatever. It is from the combinations of an atom with one or more dissimilar atoms, kations with anions, that we can deduce the color of the atoms themselves. At the outset, the following proposition must be established, namely, that in any colored inorganic compound in solution the color belongs essentially to the metallic atom, whether it exists in a free state as an ion or combined with a dissimilar atom or atoms to form a molecule. In other words, the color does not belong to the ion with exclusion of the molecule, nor to the molecule with exclusion of the ion. Color when it appears is the essential property of the atom, possessed by it in the free state and carried by it into any electrolyte which it forms. For proof of this the author cites the experiments of Glan and of Ewan, using copper sulphate solutions of different dilutions and noting the absorption. This was found to be the same when the light passed successively through distilled water and the solution and when it passed through the two mixed together. Since the dissociation was twice as great in the second case, it is clear that if the color depended on the ions only the absorption would have been more than doubled, while if it depended on the molecules only it would have been materially decreased. Hence it is obvious that the color belongs to the atom, whether it exists as an ion or whether by union with a dissimilar ion it forms part of an electrolyte. As criteria for determining the colors of ions the author uses the following: (1) When an electrolyte gives a dilute solution in water which is colorless, both the kation and the anion are colorless. Thus, since lithium bromide solution is without color, the ions of both elements are also colorless. So, too, since no relation exists between the color of an atom and that of its molecule, we find that the two colorless bromine atoms form the intensely colored element bromine. (2) When an electrolyte gives a colored dilute solution in water the constitution of the anion must first be considered. If it is a single atom, then the color of the solution belongs entirely to the kation, since all elementary anions are colorless. (3) Even when the anions is composite, conclusions may be drawn. In the case of sulphates, for example, whose anion is composite, colored dilute solutions likewise owe their color to the kation. These criteria afford the means of deciding upon the color of the entire series of elementary atoms. For the present purpose, however, it is not necessary to inquire what that color is, but only whether color is present or not.

Upon the results thus obtained the author founds, first, a new classification of the elements based on more correct principles than those previously made use of, and, second, a proof that the color or non-color of an element is a function of its atomic weight. Considering the elements numerically, it appears (1) that those whose atomic weights are less than 47 have colorless ions only; (2) that colored ions suddenly commence with titanium (48) and form an unbroken series of eight elements up to copper (63.4); (3) that a series of nine metals follows having colorless ions only, beginning with zinc (64.9) and ending with yttrium (92.5); (4) that next comes six metals with colored ions extending from niobium (94) to silver (107.7); (5) that these are followed by nine metals having colorless ions, from cadmium (111.6) to lanthanum (139); (6) that next come ten metals having colored ions, from cerium (142) to gold (196 2); (7) that the six remaining metals are alternately colorless and colored, mercury (199.8) being colorless, thallium (203.6) colored, lead (206.4) colorless, bismuth (210) colored, thorium (234.?) colorless, and, finally, uranium (240) colored. From the conception of the all-important nature of the color of the atom, while that of the element is of little significance, the author draws several interesting conclusions: First, that the well-known Periodic law must be rejected as based on erroneous principles; and, second, that *no element having ions colored at all valencies can belong to the same natural group with elements having colorless ions only.* This law, which he calls the Law of Color, is rigorous and fundamental; rigorous, because it admits of no exception; fundamental, because it divides elements into two chief divisions, with strongly marked differences.

As has been shown, the mass of the elements may be separated into two great divisions, those with ions always colorless and those with ions always colored. These two groups are always distinct, the elements in one having no relation with those in the other—*i. e.*, we never find in natural groups elements belonging to more than one of these two great divisions. If we arrange in the first division the elements whose ions are always colorless, placing them in numerical order in vertical columns of nine each, and then if we read the horizontal lines, we shall find that "*the entire class of elements with colorless ions is divided into nine great groups*," all absolutely natural, each element accurately fitting in its proper place. The table thus made includes all those elements whose ions function as anions with part of the kations. If the series of elements having all their ions colored be arranged in a second similar division, they fall into four series, the members of which have their atomic weights immediately following each other in unbroken succession. Intermediate between these two divisions is a small class of eleven transitionals, having ions which at some valencies are colored and at others colorless. The relations of this peculiar group are chiefly with the elements having colorless atoms only. With those having atoms always colored their relations are slight; but they have been given a place in the table with the latter to emphasize the fact "that in the entire series of elements *there is not a single case in which an element having atoms always colorless appears in the regular numerical series between a transitional element and one with atoms always colored. Also that there is not a single case in which an element with atoms always colored appears in the numerical series between a transitional element and one having colorless atoms only.*" This mixed group contains elements whose atoms function as kations only.

The paper concludes with a discussion of the periodicity of the law of color, illustrated by a plate, commencing with hydrogen and showing a double series of eighteen elements, with increasing atomic weights, all having colorless ions only. Approaching the first of the colored groups—*i. e.*, the iron group—we find the transitional elements titanium and vanadium, which have both colorless and colored ions, the former uniting them to the preceding and the latter to the following series. This alternation is continued through the list of the elements, showing that with atomic weights from 1 to 47, from 65 to 90, and from 112 to 139 their atoms are colorless; from 52 to 59, from 103 to 106, from 145 to 169, and from 192 to 196 the atoms are always colored. Elements whose place in the numerical series falls between these periods have both colored and colorless atoms. The six remaining metals have colorless and colored atoms alternately. Evidently the conclusion drawn by the author from these facts, "that the color of the elementary atoms is to a large extent a *function of their atomic weights*," is fully justified.

In his second paper, read before the National Academy the following year, Mr. Lea considers more in detail certain consequences of his general theory. The law of the interaction of ions he states thus: "If a colored substance be formed by the union of a colorless kation with a colorless anion, the color belongs to the molecule only. The colorless ions have so modified each other's vibration periods that selective absorption is exercised. As soon therefore as the molecule is divided into ions the color must disappear; consequently if we find a solvent, which, like water, is capable of separating the ions, the resulting solution when dilute must be colorless, no matter how intense the color of the compound." The truth of this law he experimentally tested, and found the results confirmatory without exception. With regard to the combinations of ions, he states as follows: A, two or more similar colorless ions may unite to form a colored elementary molecule; B, two or more similar ions, colored, may unite to form a colorless (or white) molecule or polymer; C, two or more similar colored ions may unite to form a molecule of a wholly different color; D, two or more dissimilar colorless ions may unite to form a colored molecule. No ion, and therefore no atom, is black, but is always transparent to some portion or portions of the visible rays; atoms and ions differing absolutely in this respect from molecules. In considering the theory of the action of acid indicators he maintains that dissociation has no essential connection with their reactions. The fact simply is that by combining with alkalies these substances either have their color much intensified or change it altogether. From the results of his color investigations Mr. Lea draws the following general conclusions: (1) When highly colored inorganic substances are composed of colorless ions, then if these substances can be brought into solution as electrolytes, the color wholly disappears. (2) The union of ions, colored and colorless, gives rise to the most surprising changes of color. (3) The change of color of an acid indicator placed in contact with an alkali in no way depends upon dissociation. (4) Selective absorption of the visual rays by an element can never constitute a basis for classification, but the relation of ions to the visual rays leads to a classification which is in absolute harmony with the chemical characteristics of the elements. (5) While there is good reason for believing that in solution the ions are separated so as no longer to affect each other's vibrations, it is also certain that they remain within each other's range of influence, so that they cannot be considered as free.

If I have been at all successful in presenting the salient points of the scientific life of Matthew Carey Lea, it will be clearly evident that he was a most industrious worker in the profounder regions of his favorite science. He was not only an observer of the acutest type, but he was at the same time thoroughly acquainted with the literature of chemistry, both past and present; so that he was readily able to appreciate to the full the real significance of the observations which he made and to use these observations to the best advantage. His power of work was well nigh unequaled and he was ever indefatigable in experimental research. Moreover, his memoirs greatly impress the reader with his exceptional candor. He was always conscientiously critical concerning himself when at work in his laboratory. The skill with which he planned and executed his experiments is equaled only by the intense love of truth which he showed in his criticism of them. He never expressed an opinion without having the facts in hand on which to base it, and in his papers he always gives the fullest and clearest details of his methods of work. In all the multifarious directions in which he studied and experimented he was ever most careful to treat those with whom he differed with the utmost courtesy. No one could differ from him on any matter without seriously questioning his own position on the subject in dispute.

Obviously this unremitting labor and this earnestness and honesty of purpose could not fail of its reward. He became an acknowledged authority on all the subjects he had sought to make his own. His opinion was recognized as the final opinion in photographic chemistry, both in this country and in Europe. He was everywhere regarded as the pioneer investigator in the more scientific realms of the art, and his studies on such subjects as the preparation of collodio-bromide emulsions, on the chemistry of developing agents, on the influence of color on the reduction by light of silver salts, especially the haloids, and particularly his work on the remarkable tendency of these substances to form colored compounds practically of all possible hues, and so foreshadowing the success of heliochromy in a not remote future—these studies must ever be considered the most valuable contributions to the science of photography made during the last quarter of a century in which he lived. His remarkable acuteness, for example, in suggesting the existence of what he so happily characterized as photosalts is equaled only by the analytical ability with which, sometimes by direct and sometimes by indirect methods, he finally fully established them. The possibility of hemisalts as he called them—salts which in the free state are extremely difficult, if not impossible, to isolate, but which readily form well-marked and very stable compounds with their normal or mono-allies—at first only a shrewd conjecture, became in his skillful hands an accomplished scientific fact. And his convincing proof that ordinary silver chloride is capable of combining with silver subchloride to form the photochloride of silver, and that this is the substance which constitutes the latent photographic image, is paralleled only by the experimental evidence he furnished that the action of light is not necessary to its production, but that it may be made by a variety of purely chemical and even mechanical processes.

Besides his scientific work, Mr. Lea was devoted to literature and the classics. In fact, he was an exceptionally good linguist, and therefore was constantly familiar with all that was best in the European languages.

In early manhood he met with an accident in his laboratory, which seriously injured one of his eyes, and which eventually required its removal. He was able, however, to keep up his interest in the current work of foreign literary scholars through the devotion of his wife, who for many years read to him constantly.

Although he was naturally retiring in his disposition and, owing, no doubt, to his continued ill health, lived the life almost of a recluse, yet his intimate personal friends bear willing testimony to his brilliance as a conversationalist. He belonged only to a few scientific organizations. In 1848 he connected himself with the Franklin Institute, taking a special interest in the Chemical Section. In 1895 he was elected a member of the National Academy of Sciences.

On the 14th of July, 1852, Mr. Lea married his cousin, Elizabeth Lea Jaudon, at that time the widow of William Woodhouse Bakewell, of New Orleans. She died on the 19th of March, 1881, leaving an only son, George Henry Lea, who is still living. His second wife was Eva Lovering, the daughter of Professor Joseph Lovering, of Cambridge, Mass., by whom he had no children.

Toward the close of his life he was seriously troubled with an affection of the prostate gland, causing intense suffering, and finally requiring an operation. Though apparently successful at first, his strength at his advanced age was not equal to the strain put upon it, and he died at his residence, at Chestnut Hill, on the 15th of March, 1897, in the seventy-fourth year of his age.

His large and valuable collection of books and apparatus was bequeathed to the Franklin Institute, together with a fund in perpetuity for the purchase of books and journals. Throughout his life he was a constant donor to charities of many kinds, a goodly number of the most prominent charitable organizations in his native city being handsomely remembered in his will.

LIST OF THE MORE IMPORTANT SCIENTIFIC PAPERS OF MATTHEW CAREY LEA.

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25. On Methylamine. *Am. J. Sci.*, II, xxxiii, 366, 1862.
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