January 15, 1857.

The LORD WROTTESLEY, President, in the Chair.

The following communications were read :—

I. "Photo-chemical Researches.—Part II. Phenomena of Photo-chemical Induction." By Prof. BUNSEN of Heidelberg, and HENRY ENFIELD ROSCOE, B.A., Ph.D. Communicated by Prof. STOKES, Sec. R.S. Received November 27, 1856.

(Abstract.)

Chemical affinity, or the force which regulates the chemical combination of two bodies, is like all other forces, a certain definite quantity. Hence it is erroneous to say, that under different circumstances the same body can possess different affinities; more correctly we should say, that in the one case the bodies are able to follow the chemical attraction of their molecules, whilst in another case opposing forces render this combination impossible. These opposing forces may be considered as resistances similar to those exerted in the passage of electricity through conductors, in the distribution of magnetism in steel, and in the conduction of heat. We overcome these resistances when by agitation we increase the formation of a precipitate, or by insolation effect a decomposition.

We call the act by which these resistances to combination are lessened, and the formation of a chemical compound promoted, "chemical induction;" and we specify this as photo-chemical, thermo-chemical, electro-chemical, or idio-chemical, according as light, heat, electricity, or pure chemical action is the force which promotes the combination.

The phenomena of photo-chemical induction are particularly interesting, as affording starting-points from which we may gain a knowledge of this mode of action of affinity.

That on exposing a mixture of chlorine and hydrogen to the light the action does not commence to its full extent at once, was observed

by Draper in 1843. An explanation of this fact was given by the supposition that the chlorine underwent on insolation a permanent allotropic modification, in which state it possessed more than usually active properties. This explanation is, as we shall show, erroneous, and the whole phenomenon is caused by the peculiar action to which we have given the name of photo-chemical induction. When the standard mixture of chlorine and hydrogen is exposed to a constant source of light, no action is at first perceptible; after a short time, however, the action becomes visible, and gradually increases until a constant maximum is reached. Experiments made with different amounts of light from different luminous sources, showed that the times which elapsed from the beginning of the exposure until the maximum was obtained, varied very much, according to circumstances. In one case the maximum action was reached in fifteen minutes, in others after an exposure of three and four minutes. The first action was in one case visible after six minutes' insolation, in others after one minute, whilst in some experiments a considerable action was observed in the first minute.

The condition modifying the action of the induction which we first examined, was the action of the mass of the insolated gas. From various experiments, it was found that the duration of the induction increased with the volume of exposed gas (by constant amounts of light), and curves have been drawn, representing the increase of the induction for the various volumes of gas employed.

We next examined the dependence of the duration of induction upon the amount of light to which a constant volume of gas was exposed, and experiment showed—

1. That the time necessary to effect the first action of the photo-chemical induction decreases with increase of light, and in a greater ratio than the increase of light.

2. That the time which elapses until the maximum is attained also decreases with increase of light, but in a much less ratio.

3. That the increase of the induction proceeds at first in an expanding series, attains a maximum, and then converges when the true maximum action is attained. The law regulating the increase of the induction by increase of light, we have rendered visible by curves.

The results of these experiments suggested the question, Is this

condition of increased combining power, into which the mixture of chlorine and hydrogen passes by insolation, permanent, or is it confined to the time during which the gas is exposed to the light? In order to determine this question, the sensitive gas, which had stood for some time in the dark, was exposed to a constant source of light, and the time noted which elapsed before the maximum action was reached; the apparatus was then darkened for one minute, and then again insolated, and the time watched until the maximum action was again observed. These observations were repeated several times, each period of darkening being longer than the preceding. Thus conducted, the experiment led to the important conclusion, that the resistance to combination overcome by the influence of the light is soon restored when the gas is allowed to stand in the dark. Curves expressing the effect produced on induction by darkening, and by exposure to light, have been drawn.

We have explained the fact, that the mixture of chlorine and hydrogen does not combine in the dark, by the supposition of the existence of a resistance to combination which is overcome when the gaseous mixture is exposed to light. This resistance to combination can be increased by various circumstances. The presence of a very small quantity of foreign gas in the standard mixture of chlorine and hydrogen is sufficient to cause the resistance to be increased to a very great extent. An excess of $\frac{3}{1000}$ of hydrogen over that contained in the normal gas, reduced the action from 100 to 38.

In these experiments we have to do with the purest form of the so-called catalytic actions, to which the photo-chemical phenomena are closely related. The quantitative estimation of the relations which exist in the phenomena of contact, between the mass of the substance the time and other modifying conditions, has not as yet been possible, owing to the absence of any case in which these relations are exhibited in their simplest form. Our method of photo-chemical measurement points out a direction which promises to afford interesting results concerning these quantitative relations; but in this communication we restrict ourselves to the consideration of these phenomena in so far as they influence the action of photo-chemical induction, intending on a future occasion to enter more fully into the new field of research indicated.

The contact action of foreign gases is still more strongly seen in

the case of small quantities of oxygen. This gas, when present in quantities amounting only to $\frac{5}{1000}$ of the total volume of gas, diminishes the action from 100 to 4·7, whilst $\frac{13}{1000}$ reduced the action from 100 to 1·3. Excess of chlorine acted in a similar manner, though not to so great an extent, $\frac{10}{1000}$ of this gas reducing the action from 100 to 60·2, and $\frac{180}{1000}$ from 100 to 41·3. On examining the effect of small quantities of hydrochloric acid gas upon the induction maximum, we found, fortunately for the accuracy of the indications of our instrument, that an amount of $\frac{1\cdot3}{1000}$ of this gas does not produce any appreciable effect on the action of the induction. Uninsolated gas was found to act similarly on the normal mixture, the admission of $\frac{6}{1000}$ of non-insolated gas reducing the action from 100 to 55. Curves have been drawn, representing the relation between the action and the amount of foreign impurity introduced. Several series of experiments also showed that a mixture of chlorine and hydrogen, which was so nearly pure that no alteration of the maximum action was observable, was longer in attaining the maximum than the perfectly pure gas; hence the duration of the induction serves as an exact measure of the absence of all foreign gases in the standard mixture.

An explanation of the laws of photo-chemical induction derived from the above-mentioned experiments, might easily be found in the assumption that the chlorine or the hydrogen, or both gases, undergo upon exposure to light a change similar to that between common and ozonized oxygen, or that these two gases can, under certain circumstances, be invested with active, and, under other circumstances, with passive properties. If this hypothesis be true, each gas must undergo this peculiar modification when separately exposed to the action of the light. That this is not the case was shown by the following experiment:—The two gases were separately evolved, and each led through a long glass tube, in which they could be separately exposed to the action of diffuse and direct sunlight. After this exposure, the gases passed through a connecting tube into the apparatus, in which a constant source of light gave the duration of the induction. Thus alternately insolating and darkening the separated gases, we observed the effect on the gases subsequently mixed and exposed to lamplight. No difference was perceptible in the duration of the induction between the gases previously insolated and those

evolved in the dark. Hence we may conclude, that the light does not effect a permanent modification, either of the chlorine or hydrogen, but that the combination produced by the light must depend on photo-chemical action affecting only the increasing attractions of the chemically active molecules.

All the curves representing the increase of the induction under various conditions have a common form, and a point of flexure at which the maximum increase occurs. In order to determine whether this common property of the curves arises from the general mode of action of affinity, or whether the light plays an essential part, we have made experiments upon idio-chemical induction, *i. e.* action in which pure chemical attractions alone effect the alteration. For this purpose we employed a dilute aqueous solution of bromine with tartaric acid, which mixture, when left to itself in the dark, undergoes decomposition, hydrobromic acid being formed. By determining the amount of free bromine contained in the liquid at different times, we became acquainted with the rate at which the decomposition occurred. Analysis showed that the amount of hydrobromic acid formed was not the same in equal spaces of time; and curves representing this increase were found to have the form obtained for the photo-chemical induction. Hence the cause of this maximum increase appears not to lie in any peculiar property of light, but rather in the mode of action of affinity itself.

One of the many interesting applications of the laws of photo-chemical induction relates to the phenomena of photography. As an instance of this application we cite the remarkable observations of Becquerel, which induced him to assume the existence of certain rays which can continue, but not commence, chemical action. In order to explain the phenomenon observed by the French physicist, we do not need to suppose the existence of a new property of light, as the facts are easily explained by the laws of photo-chemical induction; and we are satisfied that these relations, which we have examined only in the case of chlorine and hydrogen, occur in a slightly modified form in other photo-chemical processes.

Having determined in this part of our investigation the most important phenomena of photo-chemical induction, we shall in the next section consider the laws which regulate the chemical action of light after the induction is completed.