

LV.—*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*

By DAVID LEONARD CHAPMAN and LEO KINGSLEY UNDERHILL.

WHEN the conditions are such that a chemical change in a system can take place only under the influence of light, the velocity of the change is known to be proportional to the light absorbed by the coloured constituents of the system in unit time, provided that the character of the light and the composition of the system be fixed. If the light be monochromatic and the composition of the system be variable, the velocity of chemical change will be given by the numerical value of an expression of the form:

$$k_n E_n f_n(c_1, c_2 \dots),$$

in which E_n is the light energy, of frequency n , absorbed in unit time, k_n is a number the value of which depends on the vibration frequency, and $f_n(c_1, c_2 \dots)$ is an unknown function of c_1, c_2 , etc., the concentration of the constituents of the mixture, and possibly also of n .* It is assumed that the function in question is independent of the vibration frequency of the light, the rate of chemical change in a system illuminated by composite light would be given by the expression:

$$f(c_1, c_2 \dots) \int k_n \frac{dE_n}{dn} dn,$$

the limits of the integral being the maximum and minimum values of the vibration frequencies of the composite light.

In order to determine experimentally the nature of the function f the value of the integral $\int k_n \frac{dE_n}{dn} dn$ must during the course of the experiment be determinable at any moment, or be constant. By preference it should be maintained constant.

Unfortunately, in several investigations that have been undertaken with the object of estimating the influence of mass on photochemical changes the energy integral was not maintained constant, nor was any attempt made to estimate and to introduce a correction for its variation during the course of the reaction. M. Wilderman's experiments (*Phil. Trans.*, 1902, **199**, 337) on the interaction of carbon monoxide and chlorine, for example, were vitiated by this source of error. Mixtures of carbon monoxide and chlorine

* It is probable, but by no means certain, that f is independent of n . It has been invariably assumed that such is the case, although the published experimental evidence which supports the assumption is not entirely satisfactory.

enclosed in a vessel of 3.5 cm. diameter were exposed to light, and the rates of union of the gases, determined from readings of the variations in pressure, taken at stated intervals of time, the readings being continued until a considerable proportion of the chlorine originally present had disappeared. Under such conditions the light absorbed must have diminished considerably during the progress of the experiment, and the conclusion drawn by Wilderman from his uncorrected measurements, namely, that the chemical change in question is bimolecular, and conforms to the same law of mass as a purely idiochemical change, cannot therefore be accepted as valid. Strictly, his experiments can be taken only to indicate that, under conditions which would secure a constant rate of absorption of light, the order of the change would be lower than the second.

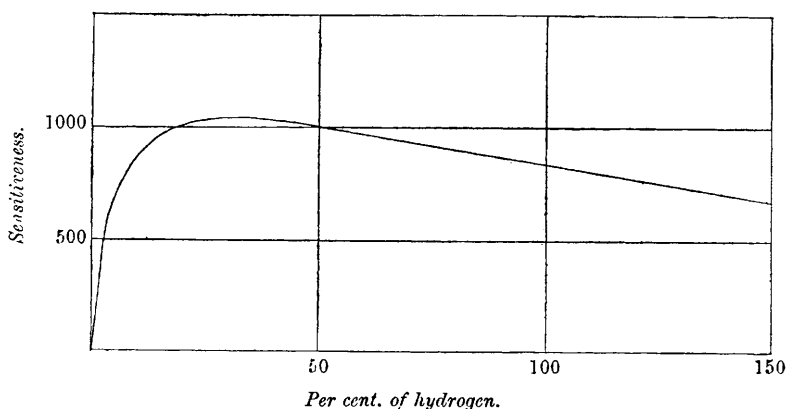
At first sight it might appear that the photochemical interaction of carbon monoxide and chlorine would be a particularly suitable change to investigate with the object of estimating the influence of mass on the velocity of a photochemical transformation; but in practice we have found that a serious obstacle is presented to its investigation owing to the difficulty of obtaining mixtures of the gases containing only such inhibitive impurities as are not slowly changed or destroyed by the influence of the light as the action proceeds. The impurities in question are contained in the carbon monoxide, and we have up to the present failed to effect their complete removal, in spite of numerous attempts by various methods. Accordingly we have had to fall back on the action between chlorine and hydrogen. Although the rate of interaction between these gases cannot be measured with such ease as that between chlorine and carbon monoxide, yet the mixture can, with the exception of oxygen (which does not alter in amount under the influence of light), be obtained uncontaminated with impurities which retard the change.

Our object has been to investigate, in the first place, the influence of the concentration of the hydrogen on the rate of formation of hydrogen chloride. The partial pressures of the chlorine and of the oxygen in the mixtures examined in one series of experiments were therefore kept constant, whereas that of the hydrogen was varied. A small amount of oxygen was added to the chlorine in order to make it quite certain that the mixtures rich in hydrogen did not contain an appreciably larger proportion of oxygen than those poorer in hydrogen, as would otherwise have been the case if the hydrogen had adventitiously, or as a result of its method of preparation, contained a trace of oxygen. The intensity of illumination was always the same, and, as the concentration of the

chlorine was also invariable, the energy absorbed by the different mixtures in unit time was constant.

It was found that as the partial pressure of the hydrogen was increased from zero the rate of formation of hydrogen chloride was at first almost proportional to the partial pressure of the hydrogen; but the ratio of partial pressure of hydrogen to velocity of interaction rose continuously in value as the proportion of hydrogen was increased, and when the pressure of hydrogen had attained a definite value the rate of formation of hydrogen chloride became a

FIG. 1.



maximum. Then, as the proportion of hydrogen was still further increased, the rate of interaction of the chlorine and hydrogen fell very slowly. If the percentage of hydrogen is plotted against the sensitiveness, a curve of the form shown in Fig. 1 is obtained.

Results of the character just indicated were not unexpected, and, indeed, they admit of a simple explanation with the aid of the theory of photochemical change formulated in previous papers. They appear, however, to be at variance with views recently expressed by Weigert (*Ann. Physik*, 1907, [iv], **24**, 155 and 243) on the nature of photochemical changes of the class under consideration. It is desirable that the bearing of our results on these views should be briefly considered.

Weigert, from certain observations made while he was investigating the interaction of chlorine and carbon monoxide, arrived at the conclusion that the action of light is catalytic, or more precisely that the light generates nuclei, in the vicinity of which the latent or almost latent forces of affinity become abnormally active and are

thus rendered capable of impelling the system into the most stable state of chemical composition. If this is a complete account of the mechanism of the photochemical interaction of chlorine and carbon monoxide, and of chlorine and hydrogen, the conclusion that the rate of the action ought to be proportional to the colourless constituent of the mixture appears to be almost inevitable. This consequence of the theory, however, is obviously not in harmony with the results of our experiments, according to which the rate of interaction of the gases is nearly independent of the proportion of hydrogen when the latter exceeds a definite value. The result on which Weigert bases his theory appears to us to be a consequence of the thermodynamic principles, and therefore consistent with any mechanical hypothesis which does not contradict those principles.*

The theory about to be advanced is of limited application, in so far as it is capable at present of being verified by quantitative relations; but it will be convenient to postpone the defining of these limitations until a general outline of the theory has been presented.

The photochemical transformation of chlorine and hydrogen into hydrogen chloride is accompanied by a fall in free energy vastly greater than the light energy required to induce the change. An hypothesis capable of giving a satisfactory mechanical account of the fact that the free energy of the system cannot, without the assistance of a relatively small supply of highly efficient external energy, break up the molecules of the elements and bring into operation the force of affinity between the atoms of chlorine and hydrogen, is not likely to be discovered until a much more intimate knowledge of the internal structure of the atoms has been gained; but it is probable, we believe, that such an hypothesis might not unprofitably be sought for in the periods of free vibration of the valency electrons. We are, however, at present only concerned with the correlation of the small but necessary supply of external energy and the extent of the chemical change induced by it.

Consider the effect of exposing to light a mixture of chlorine, hydrogen, and a relatively small amount of oxygen. The light is absorbed by the chlorine, and exists for a time in the molecules of that substance as a form of energy of vibration which is incapable without further modification of promoting the union of the

* In support of his conclusions, Weigert quotes the results of Bevan (*Phil. Trans.*, 1903, *A*, 202, 71) on cloud formation in a moist illuminated mixture of chlorine and hydrogen. For comments on Bevan's conclusion, the reader is referred to the paper on the interaction of chlorine and hydrogen by Burgess and Chapman.

hydrogen and chlorine. Of this vibrational energy by far the larger part is degraded, and thereby rendered ineffective by the agency of the oxygen, the proportion thus dissipated depending almost entirely on the partial pressures of the chlorine and oxygen, and being therefore almost the same when the concentration of both of these gases is kept constant. The vibrational energy which escapes dissipation by this process is transformed into a comparatively stable and still highly efficient form, and as such is accumulated in the chlorine molecules, which are thereby rendered abnormally active. The latter form of energy which endows the chlorine molecules with chemical activity we shall for brevity call the actinic energy. If the mixture contains no hydrogen the actinic energy is dissipated, the rate of dissipation being for the same concentration of chlorine proportional to its amount in unit volume. If the mixture contains hydrogen, however, a part only of the actinic energy will be directly dissipated, the rest being utilised and degraded in the promotion of chemical change (the proportion of actinic energy lost by direct dissipation being almost zero when the concentration of the hydrogen is high).

We shall now show that the quantitative results are in accordance with the above view of the mechanism of the change. To this end we shall deduce from the theory what ought to occur in an element of volume of a system composed of chlorine, hydrogen, and oxygen under the influence of light. Let U be the light energy absorbed in unit volume by the chlorine in unit time, and let V be the vibrational energy in unit volume. The vibrational energy supplied in unit time by the light is obviously U , whilst that lost in unit time by dissipation is given by CV , C being a function of the concentration of the chlorine and oxygen. In the steady state the gain and loss of V must be equal, or $V = U/C$. The actinic energy acquired by the chlorine in unit time is proportional to V , and since $V = U/C$ it must be given by kU , k being a function of the concentration of the oxygen and chlorine. The actinic energy in unit volume being denoted by X , the amount dissipated in unit time is obviously proportional to X , and may therefore be put equal to cX (c being a constant), whilst that which is degraded in bringing about the union of the chlorine and hydrogen is given by $K[\text{H}_2]X$, in which K is a constant, and $[\text{H}_2]$ the concentration of the hydrogen.

Accordingly, $dX/dt = kU - cX - K[\text{H}_2]X$.

But in the steady state which is attained in an immeasurably short period of time after the commencement of the illumination $dX/dt = 0$.

$$\therefore kU = cX + K[\text{H}_2]X.$$

The last term on the right hand side of the equation is equal to the actinic energy employed in unit time in converting chlorine and hydrogen into hydrogen chloride, and the rate of formation of hydrogen chloride may be taken as proportional to the magnitude of the same term, if we may assume—the justification for the assumption cannot be conveniently given until later—that for photochemical changes of the class to which the interaction of chlorine and hydrogen belong, the hydrogen chloride formed is proportional to the actinic energy required for its production.

When the concentration of the hydrogen is small, $kU = cX$, and therefore $X = kU/c$.

Accordingly, the rate of formation of hydrogen chloride is approximately proportional to:

$$kKU/c[\text{H}_2].$$

Now kKU/c is constant when the concentrations of the chlorine and oxygen, and the intensity of illumination, are kept constant—as they were in one series of our experiments—and, therefore, under such conditions the rate of formation of hydrogen chloride ought to be proportional to $[\text{H}_2]$ when $[\text{H}_2]$ is small.

When the concentration of the hydrogen is relatively large,

$$kU = K[\text{H}_2].X,$$

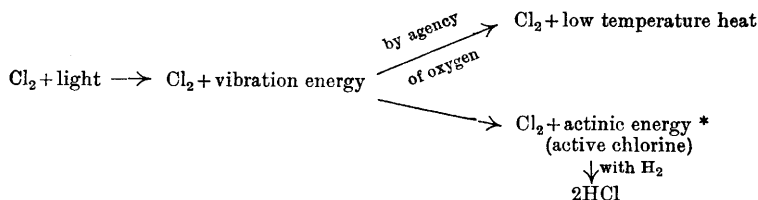
the interpretation of which is that the rate of formation of hydrogen chloride ought to be approximately constant, when the light absorbed and the partial pressures of the chlorine and oxygen are kept constant as they were in a series of our experiments.

It will be seen that the experimental results are in general agreement with the requirements of the theory. It only remains to account for the gradual fall in the rate of interaction of the chlorine and hydrogen when the pressure of the hydrogen is increased from a given limiting value. We believe that this fall is due to the circumstance that hydrogen, like oxygen, is capable, although in a very limited degree, of degrading the vibrational energy from which the actinic energy is derived.*

The transformations conceived to take place in the energy associated with the chlorine molecules, and the subsequent formation of hydrogen chloride, can be conveniently summarised with the aid of the following scheme:

* The fact that hydrogen diminishes, in a relatively slight degree, the phosphorescence of iodine vapour can be advanced in support of this view.

In the expressions developed above, the effect of the slight degradation of vibrational energy by hydrogen has been left out of account.



It is probable that the vibrational energy is composite, and that its character depends on the nature of the stimulating light. This question is at present under investigation.

At first sight it may not be obvious why it has been assumed that the chlorine can be associated with two distinct kinds of efficient energy designated respectively the vibrational energy and the actinic energy, the latter (to which the union of the chlorine and hydrogen is due) being derived from the former (which is degradable by oxygen, but incapable of effecting the union of the chlorine and hydrogen). The reason is that if the chlorine were associated with one kind of energy only—the vibrational energy—(which must be supposed to be both degradable by oxygen and effective in bringing about the union of chlorine and hydrogen), then clearly the rate of formation of hydrogen chloride ought continuously to approach a maximum value independent of the concentration of the oxygen as the relative proportion of impacts of chlorine molecules with oxygen and hydrogen molecules respectively is diminished, that is, as the concentration of the hydrogen is increased, that of the oxygen being constant. Whereas, of course, the maximum sensitiveness attained increases rapidly as the oxygen is diminished.

An alternative hypothesis, which is probably no more than a special case of the foregoing, is the following. The fraction of the vibrational energy which is not dissipated by the agency of the oxygen converts some of the chlorine into a very unstable and active allotropic modification, which is capable of reacting with hydrogen. If a sufficient number of hydrogen molecules are present in unit volume of the mixture practically every active chlorine molecule generated by the influence of the light makes a fruitful impact with a hydrogen molecule, and since the number of active chlorine molecules produced is proportional to the light absorbed, the hydrogen chloride formed under these conditions will also be proportional to the light absorbed. If, however, the hydrogen

* It is possible that Strutt's active form of nitrogen consists of ordinary molecules of nitrogen rendered active in the same way as we conceive that chlorine molecules are rendered by the agency of light.

molecules are scarce, most of the active chlorine molecules will, on account of their extreme instability, revert to inactive molecules, and only a small number of them will make fruitful impacts, the percentage of active molecules which make fruitful impacts being proportional to the concentration of hydrogen.

It is now desirable that we should examine a little more closely the energetics of the hydrogen-chlorine reaction. We shall, thereby, be enabled to offer further justification for our main assumption, namely, that the quantity of actinic energy and the amount of chemical change induced by it are equivalent, or, in other words, that the decrease in X attributable solely to the formation of hydrogen chloride is proportional to the hydrogen chloride produced. We shall be enabled also to define the class of chemical change to which the same assumption may be legitimately applied.

It is a simple matter to show that the fall in free energy during the formation of two gram-molecules of hydrogen chloride is given by the expression :

$$Rt \left(\log_e \frac{[\text{HCl}]^2}{[\text{H}_2]' [\text{Cl}_2]'} - \log_e \frac{[\text{HCl}]^2}{[\text{H}_2] [\text{Cl}_2]} \right),$$

in which a symbol enclosed in square brackets signifies the concentration of the gas corresponding with the symbol, and a square bracket with a dash indicates a concentration in a system in equilibrium.

If $[\text{HCl}]'$ is made equal to $[\text{HCl}]$, the expression reduces to :

$$Rt \log_e \frac{[\text{H}_2] [\text{Cl}_2]}{[\text{H}_2]' [\text{Cl}_2]'}.$$

Now in ordinary circumstances the product $[\text{H}_2]' [\text{Cl}_2]'$ is extremely small in comparison with $[\text{H}_2] [\text{Cl}_2]$, and therefore the numerical value of the above expression is large, and will be very little affected by very appreciable alterations in either $[\text{H}_2]$ or $[\text{Cl}_2]$.

Accordingly, the efficient energy in the system itself available for the purpose of converting the chlorine and hydrogen into hydrogen chloride is almost constant, that is, is almost independent of the pressure of the hydrogen or chlorine. In other words, the tendency of the chlorine and hydrogen to change into hydrogen chloride is almost independent of the partial pressure of the former gases; and, therefore, if in addition to the energy of the system a small quantity of energy of greater efficiency than that contained in the system is required to bring about a definite amount of chemical change, the quantity of additional energy will be constant, it being assumed, of course, that its quality is the same. Our principal assumption could not be made for a system near the condition of equilibrium since in that case a small variation in the concen-

tration of one of the interacting constituents would appreciably alter the tendency of the change to take place in a given direction, and therefore the additional supply of actinic energy required to bring about a stated amount of chemical change would not be independent of the constitution of the system.

It will consequently be perceived that without modification the above theory can only apply to photochemical changes of the same class as that under consideration, namely, to those changes which are attended by a considerable fall of chemical potential. It is, we believe, impossible to elaborate a satisfactory quantitative theory of the dynamics of photochemistry applicable to every class of chemical change without the assistance of much more experimental information than is at present available for the purpose.

EXPERIMENTAL.

The chlorine and hydrogen were prepared by the electrolysis of concentrated hydrochloric acid. In the preparation of the hydrochloric acid the greatest care was taken to prevent contamination with organic impurities, as these would have furnished inhibitors which could only have been removed from the interacting gases with extreme difficulty, and trustworthy actinometric measurements cannot, of course, be made so long as the chlorine and hydrogen contain the least trace of inhibitive impurity. Into chlorine-water which had been boiled for many hours hydrogen chloride was passed until the liquid was saturated. The hydrogen chloride was prepared by the action of concentrated sulphuric acid on common salt. The common salt was prepared in the usual way by its precipitation from a solution of brine with hydrogen chloride. In order to destroy organic impurities in the concentrated sulphuric acid, the latter was first heated with chlorine, and then, after sodium peroxide has been dissolved in it, boiled until the resulting persulphuric acid had been destroyed. The apparatus employed to electrolyse the hydrochloric acid has already been described (Chapman and MacMahon, T., 1909, **95**, 135).

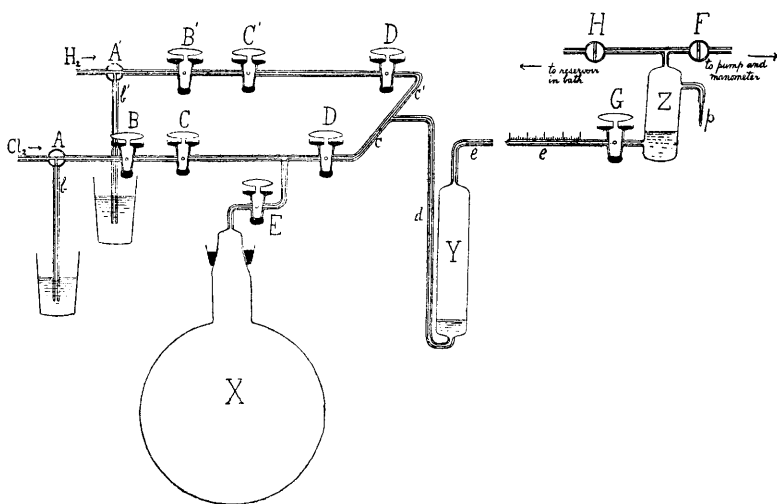
A diagrammatic representation of the essential part of the apparatus is given in Fig. 2.

X is a large globe which is used to contain the mixture of chlorine and oxygen. *Y* is the insolation vessel of the actinometer which is immersed in a large glass tank filled with water, the water being kept at a constant temperature of 20° with the aid of an electric thermo-regulator. The index tube *e* of the actinometer communicates through the tap *G* with the reservoir *Z*. By opening the tap *F* the reservoir can be brought into communication with a

water-pump and a manometer, neither of which are shown in the diagram. The reservoir is also in connexion with a large glass bottle immersed in the same tank as the actinometer, the pressure above the liquid in *Z* being thereby maintained constant.

The filling of the globe *X* was accomplished in the following way: The hydrochloric acid was electrolysed, and the chlorine and hydrogen permitted to escape through the tubes *b* and *b'* until all the air had been expelled from the cell and delivery tubes. In the meanwhile, before water had been introduced into *Y* and *Z*, the apparatus, including the globe, from the taps *B*, *B'*, and *H* to

FIG. 2.



the pump was exhausted. After closing *H*, the tap *B* was very cautiously turned just sufficiently to admit chlorine to the exhausted apparatus at such a rate that the gas did not cease to enter slowly the potassium hydroxide solution under *b*. When the pressure in the globe had risen to about 15 cm. of mercury, the apparatus was again exhausted. The operation of filling with chlorine to 15 cm. and exhausting was repeated four times. The taps *D* and *D'* were then closed, and the globe *X* completely filled with chlorine, an operation which took about six hours. The pressure in the globe was then reduced below the atmospheric pressure to an extent depending on the amount of oxygen it was desired to introduce into the globe. After the tap *E* had been closed, the potassium hydroxide solution removed from under *b*, the electrolysis of the hydrochloric acid in the cell discontinued, and the three-way tap *A* turned so that *b* communicated with the apparatus and not with

the cell, a slow stream of oxygen was passed through *b* in the direction *A*, *B*, *C*, *D*, etc., until the chlorine had been removed from the capillary tubes. The tap *E* was next opened, and the oxygen permitted to enter the globe until the pressure was again that of an atmosphere. Then the tap *E* was closed, and the oxygen and chlorine in the globe allowed to mix, a process for the completion of which it was found desirable to assign at least two days. Water which had been previously digested for many hours with chlorine was introduced into the reservoir *Z* through the side-tube *p*, which was drawn out to a capillary tube to permit of its being easily opened and closed by respectively breaking off the tip with the aid of a file, and fusing up the open end before the blow-pipe. Of the water thus introduced into *Z* a convenient quantity was admitted into the insolation vessel through the tap *G*, the pressure in the insolation vessel having been previously reduced below that in *Z*. The filling of the insolation vessel with a mixture of known composition of hydrogen and of the gas contained in the globe was accomplished in a similar manner to the filling of the globe. With *B*, *B'*, and *E* closed, and the other taps open, the apparatus was exhausted. Hydrogen was then admitted to the apparatus through *B'*, and pumped out again several times until all oxygen had been removed from the actinometer and delivery tubes. Then with the tap *D'* closed the insolation vessel *Y* was washed out several times with the gas in *X*, and then filled with the same gas. By gently shaking *Y* the water which it contained was saturated with chlorine. The pressure in *Y* was then reduced to 30 cm. of mercury, the precaution being, of course, taken to remove the excess of chlorine from the liquid. Hydrogen was then admitted to *Y* until its partial pressure had reached the desired value. This operation demanded the exercise of some care; it was accomplished by adjusting the pressure in *Z* to the required value, allowance being made for the liquid contained in the vessel, then admitting hydrogen into the insolation vessel very slowly with the tap *G* partly turned on, so that the liquid in the index *c* could only move slowly in the direction of lower pressure, and when the forward movement of the index liquid had ceased, turning the tap *G* full on, the hydrogen being shut off as soon as the index liquid had reached the zero point on the scale.

The insolation vessel of the actinometer was illuminated with a Hefner lamp. The position of the lamp was unaltered during a series of observations; but in order to secure a convenient rate of formation of hydrogen chloride the intensity of illumination was altered from series to series, being greater for mixtures which contained a larger amount of oxygen. When the mixture is exposed

to light great care must be taken that the index has come to its position of equilibrium before taking the initial and final readings of its position. Attention to this precaution is particularly necessary after the mixture has been exposed to light, as the index recedes slowly for several hours after hydrogen chloride has been formed in the insolation vessel. This apparent expansion of the gas in the actinometer after exposure to light has been found to be due to the formation of a supersaturated solution of chlorine in the liquid enclosed in the insolation vessel, and to this solution slowly giving up its excess of chlorine. The excess of chlorine passes out of solution more rapidly, of course, if the actinometer is gently shaken. The cause of the formation of a supersaturated solution of chlorine is fairly obvious. The hydrogen chloride generated by the action of the light dissolves in the surface layer of water, and in the concentrated hydrochloric acid produced the chlorine is extremely soluble. The solution of chlorine in concentrated hydrochloric acid is, however, rapidly diluted by the process of diffusion, and the chlorine being less soluble in dilute hydrochloric acid tends to escape. The relative amount of hydrochloric acid produced in unit time is obtained by dividing the product of the total movement of the index and the pressure of the gas in the actinometer by the time of exposure. The results are tabulated below:

Series.	Pressure of hydrogen Pressure of chlorine.	Pressure of oxygen in cm. of mercury.	Sensitiveness.
I.	0.485 0.894	very small " "	1000 786
II.	0.511 1.000 1.472 0.0235	0.25 0.25 0.25 0.25	1000 682 636 489
III.	0.510 1.020 1.469 0.0318	0.60 0.60 0.60 0.60	1000 734 689 431
IV.	0.510 1.536	0.60 0.60	1000 688
V.	0.521 1.579	1.20 1.20	1000 837

It will be observed from the above table that a mixture which contains equal volumes of chlorine and hydrogen is not twice as sensitive as one which contains only 3 per cent. of the latter gas.

The pressure of the chlorine was nearly 30 cm. in all the experiments. For the purpose of comparison the sensitiveness of each mixture is compared with that of the mixture in the same series which contained two volumes of chlorine to one of hydrogen. The

numbers given for the sensitiveness are the means of several determinations in most cases.

The fall in sensitiveness resulting from an increase in the proportion of hydrogen present appears to be less marked as the pressure of oxygen is increased.

It will be observed that a mixture which contains equal volumes of chlorine and hydrogen is never the most sensitive, the maximum sensitiveness being given by a mixture containing a considerably lower proportion of hydrogen.

SIR LEOLINE JENKINS LABORATORY,
JESUS COLLEGE, OXFORD.
