XVII. *Photo-chemical Researches.*—Part I. *Measurement of the Chemical Action of Light.*

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THE first and only attempt which has been made to refer the chemical action of light to a standard measure, is to be found in the researches of DRAPER. The description of the instrument and mode of observation employed by him was published in 1843, in volume xxiii. p. 401 of the 'London, Edinburgh and Dublin Philosophical Magazine.'

Even with this instrument, which as we shall show is in many respects very defective, DRAPER has succeeded in establishing experimentally some of the most important relations of the chemical action of light.

In these experiments DRAPER collected hydrogen, evolved by electrolysis, over hydrochloric acid saturated with chlorine, and to this hydrogen he admitted so much chlorine, either by diffusion from the saturated acid or by electrolysis, that the mixture consisted of nearly equal volumes of the two gases, and entirely, or almost entirely, disappeared on exposure to light. The alteration in the volume of the gaseous mixture arising from the absorption of the hydrochloric acid formed by the action of the light, was read off on a scale, and being, within certain limits, proportional to the time of exposure, served as a measure of the chemical rays.

This method affords, however, no means for correctly determining the point at which the gas collected over the acid consists of equal volumes of its constituent parts; still more, however, was the accuracy of DRAPER'S instrument impaired by not considering certain conditions, which must be fulfilled, if exact photo-chemical measurements with chlorine and hydrogen are required. The first and most essential condition, as influencing the regularity of the measurements, relates to the perfectly constant composition of the gas.

When two gases, V and V_1, having respectively the coefficients of absorption α and α_1, are mixed together in such proportions that the unit of volume contains v volumes of the one gas and v_1 volumes of the other, and when such a mixture passes through a liquid, it rapidly changes its composition, according to a complicated law, until the moment arrives when the gases absorbed by the liquid are contained in the relation of αv to $\alpha_1 v_1$. If the gaseous mixture be collected over the liquid before the relation $\frac{\alpha v}{\alpha_1 v_1}$ has been established, an exchange between the dissolved and free gases must occur, and hence the composition of the gaseous mixture must constantly alter, the variations being of a greater or less amount according as the volumes of the solvent and the free and absorbed gases increase or diminish. In the method employed by DRAPER for the preparation of his sensitive gas, the conditions necessary for obtaining this relation, $\frac{av}{a_1 v_1}$, are not even approximately attained, so that from this cause alone, an exact agreement between the indications of the Tithonometer cannot be possible.

Another source of more considerable error is to be found in the alterations of pressure to which the liquid and the gaseous mixture are subjected during the whole course of the observations. This variation of pressure causes a certain quantity of gas to escape from solution in the liquid, and as the atmosphere in the liquid has a different composition from that above it, the relation between the chlorine and hydrogen will be altered, and all regularity in the indications of the instrument impaired.

As we were unable, from the foregoing reasons, to employ the mode of observation used by DRAPER, we were compelled to seek for some new method, free from the errors above alluded to.

With this object we have been obliged to examine all the circumstances which could possibly affect the combining power of chlorine and hydrogen, in a series of experiments which have extended over a long space of time, and in which difficulties of no ordinary kind have had to be overcome. For this purpose we required a mixture composed of equal volumes of chemically pure chlorine and hydrogen gases. Amongst the various methods which presented themselves for the preparation of such a mixture, that by electrolysis of aqueous hydrochloric acid appeared at first sight the least likely to give the wished-for result, as DRAPER especially mentions in his research that the electrolysis of this acid, however long continued, never yields equal volumes of chlorine and hydrogen. A series of careful experiments has however proved, most distinctly, that DRAPER'S statement is erroneous; and we have found that the electrolytic chlorine and hydrogen mixture not only consists of exactly equal volumes of chlorine and hydrogen, but that it is perfectly free from oxygen and all oxides of chlorine which might have been formed by secondary electrolytic action.

As the possibility of executing accurate photo-chemical determinations entirely depends upon this purity of the gas, we deem it necessary here to detail the experiments made upon this subject.

When a current from three or four common-sized carbon-zinc elements is passed, by means of carbon-poles, through hydrochloric acid of about specific gravity 1·148, all the chlorine set free at the anode is first absorbed by the liquid. After a short time the evolution of chlorine becomes visible, and gradually increases, whilst the colour of the liquid becomes deeper, until a point is attained, more or less quickly according to the intensity of the current and the quantity of hydrochloric acid employed, at which a statical equilibrium between the free gases and those absorbed in the liquid ensues. From this point forwards the composition of the free and absorbed gases remains constant, provided that the temperature and pressure do not vary, and the amount of hydrochloric acid contained in the liquid electrolyte does not diminish below a certain amount. The composition of the absorbed gaseous mixture varies with every change of temperature, whereas the composition of the free gas remains the same for all temperatures, provided that the statical equilibrium is not disturbed by alteration of the temperature and pressure during the evolution of the gas.

After the statical equilibrium has been established, the gas invariably contains one volume of chlorine to one of hydrogen. This important fact, which is strictly conformable to the laws of gas absorption, is deduced from the following analyses made with electrolytic chlorine and hydrogen evolved both from carbon and platinum poles of different dimensions, by currents of various degrees of intensity. In order accurately to measure the volume of gas required for analysis, we allowed the dried electrolytic gas to pass through the glass cylinders represented in Plate XVII. fig. 1. These cylinders, of the same diameter, but of various lengths, are closed by surfaces of plate glass pressed upon the ground ends of the cylinders by means of the screws *a a a*, and the joint rendered perfectly air-tight by a thin roll of white wax squeezed flat between the two surfaces of glass. Each cylinder is furnished with a delivery- and exit-tube ground into the glass, and firmly fastened by cements of gutta-percha and gypsum. The gases passed through the cylinders until the whole of the atmospheric air was displaced; and after the height of the barometer and the temperature (which was kept constant during the experiment) had been observed, the caoutchouc joinings were closed by screw-clamps, and one of them directly opened under a solution of iodide of potassium. The solution rose immediately into the vessel and liberated a quantity of iodine exactly equivalent to the amount of contained chlorine. A volumetric analysis* of this liberated iodine gave us the amount of the chlorine contained in the gas. This amount, subtracted from the total volume of gas contained in the vessel, gave the volume of hydrogen.

If α signify the amount of iodine in grammes contained in one division of the burette, n the number of measures of sulphurous acid required for complete decolorization of the iodine liquid, t the number of divisions of the burette which represents one measure of sulphurous acid, and t' the number of divisions which must be added to the liquid to which n measures of sulphurous acid have been added until the blue colouring appears; and if the atomic weight of chlorine $Cl=221{\cdot}87$, and that of iodine $I=794{\cdot}37$, and the specific gravity of chlorine gas $s=2{\cdot}45307$, the volume of chlorine contained in the vessel in cubic centimetres is equal to

$$C=\frac{773}{s}\cdot\frac{Cl}{I}\alpha(nt-t'). \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.)$$

If the heights of the barometer and thermometer on closing the vessel were respectively P and T, and if the capacity of the vessel expressed in cubic centimetres is equal to C, the total volume of gas present, reduced to 0° C. and $0^{m}{\cdot}760$ expressed in cub. cent., is found from the equation

$$C_1=\frac{CP}{(1+0{\cdot}00366\,T)\times 0{\cdot}76}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2.)$$

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* Ann. Ch. Pharm. lxxxvi. p. 265, and Quart. Journ. Chem. Soc. viii. p. 219.

The amount of chlorine, C, subtracted from the total volume of gas, C_1, gives the volume of the hydrogen contained in the gaseous mixture. The results of a series of experiments conducted according to this method are given in the following Table:—

Series of Experiments I.

	Capacity of vessel.	Temperature. T.	Barometer. P.	n.	t.	t'.	a.	C_1.	Chlorine found. C.	Chlorine calculated. $\frac{1}{2}C_1$.
Exp. 1.	34·81	$11\overset{\circ}{\cdot}3$	0·7363	2	66·1	57·7	0·002443	32·385	16·02	16·19
Exp. 2.	34·81	11·6	0·7415	2	67·0	58·3	0·002443	32·580	16·27	16·29
Exp. 3.	190·24	11·5	0·7518	6	79·6	66·6	0·0024869	180·590	89·96	90·28
Exp. 4.	61·01	12·9	0·7393	2	71·9	15·2	0·0024869	56·672	28·15	28·34
Exp. 5.	64·27	12·9	0·7393	2	77·4	19·5	0·0024869	59·700	29·61	29·85
Exp. 6.	51·60	12·9	0·7393	2	76·7	45·7	0·0024869	47·931	23·57	23·96

The two last vertical columns show that the electrolytic chlorine and hydrogen gas invariably contains equal volumes of its constituents, and that the small variations from this proportion, which occur in these experiments, do not exceed in amount the errors of observation to which even the most accurate analytical processes are necessarily subject. These analyses show also that the gas under examination did not contain any free oxygen, for if a decomposition of the water as well as the hydrochloric acid had taken place, by which two volumes of hydrogen are disengaged for every volume of oxygen, the volume of hydrogen could not have stood to the volume of chlorine, nor to the volume of chlorine and oxygen, in the simple relation of equality; especially as the free oxygen is not estimated by the volumetric method employed. The absence of all oxides of chlorine which might have been formed by secondary action may also be deduced from the following considerations. In the electrolysis of hydrochloric acid, the liberation of every two volumes of hydrogen is accompanied by an evolution of two volumes of chlorine; in the electrolysis of water the same two volumes of hydrogen are accompanied by only one volume of oxygen. This oxygen, combined with two volumes of chlorine, gives two volumes of hypochlorous acid gas. As soon as the equilibrium between the electrolytic liquid and the evolved gas has been established, the liberated gas would contain, supposing this decomposition to occur, in six volumes, four volumes of hydrogen and two volumes of hypochlorous acid gas. These two volumes, ClO, liberate, however, just as much iodine as four volumes of chlorine. Hence the analysis would have given four instead of three volumes of chlorine, on the supposition that the whole of the chlorine combined with oxygen to form hypochlorous acid. If only small quantities of hypochlorous acid were present, a slight excess of chlorine above the normal amount would have been found, whereas experiment always gave a slight loss of chlorine. By similar reasoning, it may be proved that none of the higher oxides of chlorine can be contained as admixtures in the gas.

The perfect purity of the electrolytic gas having been thus established beyond doubt, a question of no less importance presented itself; namely, does the combination of chlorine and hydrogen take place in the dark at ordinary atmospheric temperatures, or is the presence of light a necessary condition? For the purpose of determining this question, the experiments just cited, calculated according to formula (1.), were repeated with the difference, that the analyses were made after the vessels containing the gaseous mixtures had remained for some hours in the dark. We obtained,—

Series of Experiments II.

	No.	Capacity of vessel. C_1.	Temperature. T.	Barometer. P.	n.	t.	t'.	α.	Chlorine found. C.	Chlorine calculated. $\frac{1}{2}C_1$.
21 hours in dark...	I.	190·24	11°·1	0·7265	5	92·0	59·9	0·0024869	87·57	87·38
	II.	113·03	11·1	0·7265	3	89·9	34·4	0·0024869	51·50	51·91
	III.	73·42	11·1	0·7265	2	39·8	26·0	0·0024869	33·62	33·72
2 hours in dark...	IV.	51·60	12·9	0·7393	2	76·7	45·7	0·0024864	23·57	23·96
	V.	61·01	12·9	0·7393	2	71·9	15·2	0·0024864	28·14	28·34

These experiments show, that, after standing from two to twenty-one hours in the dark, only from 1 to 1·5 per cent. of the total chlorine had disappeared. The numbers in the two last vertical columns prove clearly that the electrolytic chlorine and hydrogen mixture remains unaltered when light is excluded, and that if the small differences which occur do not arise altogether from errors of observation, still their influence on the photochemical determinations is so small that it may be entirely neglected.

Having thus assured ourselves, in the foregoing experiments, that the electrolysis of aqueous hydrochloric acid affords a simple and reliable method of preparing a gaseous mixture of perfectly constant composition, which is unalterable in the dark, but sensitive when exposed to light, it now only remained carefully to examine all the circumstances which could possibly modify the action of light on the mixture, so that in the determinations they may be either entirely removed or allowed for in the calculations.

As we do not deem it necessary here to enumerate the various preliminary experiments which at last led us to the wished-for result, but tried our patience for upwards of half a year, we proceed at once to the description of the instrument by means of which we have been ultimately enabled to exclude all disturbing causes from our determinations, and have succeeded in referring the chemical action of light, not only to a comparative, but, as we shall show in a later section, even to an absolute measurement.

The arrangement of the apparatus we have employed is as follows:—The glass tube, *a*, fig. 2, blown before the glass blowpipe, serves for the electrolysis of the hydrochloric acid, and contains two electrodes of carbon, which are connected with three or four common-sized zinc-carbon elements, C, by means of the platinum wires *bb* melted through the glass. Between this vessel *a* and the battery C, is placed the gyrotrope D, by means of which the resistance in the circuit can be at any time greatly increased; this is instantly effected by reversing the balance-wire, so that the current passes through the small decomposing cell *d* containing a very dilute acid. By including and excluding this cell from the circuit, the evolution of gas in the vessel *a* may be at any moment brought to a maximum or minimum amount. The chlorine and hydrogen mixture evolved by the current passes from the vessel *a*, through an accurately ground-glass joint rendered perfectly air-tight by a layer of water contained in the cup *g*, into the washing-bulbs *w*, partly filled with water, whence it traverses the tube furnished with the glass stopcock *h*. Between this stopcock and the horizontal tube K, is placed the vessel *i*, in which the gas is exposed to the action of the light. This insolation-vessel contains from 2 to 3 cub. cent. of water, and is attached to the tubes at either end by air-tight ground-glass joints, so that when the glass stopcock is open, the gas bubbles through the water contained in the vessel *i*, then passes into the tube K and through the water contained in the vessel *l*, and finally escapes into the condenser E, in which all the chlorine is absorbed by alternate layers of charcoal and slaked lime. When the gas is allowed to pass through the whole apparatus, the liquids contained in the vessels *a*, *w*, *i* and *l* become by degrees saturated; the composition of the free gas undergoes therefore a constant alteration, which diminishes in proportion as the liquids approach the point of saturation. As soon as this point of saturation is reached, and the equilibrium of absorption established, the composition of the free gas remains perfectly constant, and is represented by one volume of chlorine to one volume of hydrogen.

The gas in different parts of the apparatus is subject to different pressures. At the surface of the carbon-poles the gas is under a pressure of the columns of liquid in *a*, *w*, *i* and *l*; at *f*, of the columns in *w*, *i* and *l*; at *h* to the pressure of *i* and *l*; and lastly, in the insolation-vessel and in the observation-tube *ss*, to the pressure of the column of liquid in *l*. Any alteration in the pressure at any one of these parts of the apparatus causes an alteration in the composition of the free gas, and necessitates a fresh saturation, in order to regain the required equilibrium. Hence the pressure must be kept constant, not only whilst the observations are being made, as the nature of the apparatus requires, but also during the time which elapses between each set of observations. For this purpose the following arrangement was made:—As soon as the volume of gas to be employed for the observations has been shut off by closing the stopcock *h*, by which the pressure in no part of the apparatus is altered, the current of electricity is weakened by reversing the balance-wire of the gyrotrope, and thus the evolution of gas in the decomposing cell *a* is rendered very slight. This feeble current of gas, which merely serves to keep the liquids in *a* and *w* in a state of equilibrium, cannot escape by the stopcock, but finds its way through a small manometer, *m*, fused on to the tube *f* and containing water, and thence by means of a caoutchouc connector into the tube *p*, which dips under water in the bottle F. This bottle serves as a regulator of the pressure, which may at pleasure be diminished or increased by raising or depressing the tube *p* in the liquid. From this bottle, F, the gas passes into the second charcoal and lime condenser, G.

In order to protect the gas contained in the insolation-vessel from alterations of volume ensuing from external heat, either from the source of light or from the body of the observer, we have employed several arrangements of screens, which we shall more fully describe when treating of the testing of the instrument. For the sake of simplicity, in figure 2 only a part of these screens has been represented; namely, the screen L, the convex lens M, and the cylinder N, closed by plates of glass and filled with water. In all the observations, in addition to these arrangements, the double metallic screen, fig. 4, afterwards described, was employed.

The following is the method adopted for filling the apparatus. The washing-bulbs *w*, the insolation-vessel *i*, and the small vessel *l*, having been supplied with the proper amount of water, the evolution-tube *a* is filled with hydrochloric acid of about sp. gr. 1·148, and the neck carefully placed upon the ground end of the tube *f*. The lower end of the tube *a* dips in mercury, which acts as a spring, pressing the tube against the end of the washing-bulbs *f*; the upper part of the tube is surrounded by water, to prevent the platinum wires fused into the glass from being heated by the passage of the electricity. A current from three or four elements is now led through the acid by means of the gyrotrope; the mixed gases are rapidly evolved, and can pass in two directions, according to the depth to which the tube *p* dips under the level of the water in the bottle F. If the lower end of this tube is placed at such a depth in the liquid that the sum of the pressures *rr*, *vv* is larger than the sum of the pressures of the columns of liquid at *w*, *i* and *l*, the gas will pass through *f*, *w*, *h*, *i*, *l* into the condenser E, supposing, of course, that the stopcock *h* is open. If, on the contrary, the tube *p* be drawn up through the caoutchouc cap *t*, in which it moves air-tight, until the sum of the pressures of the columns *rr* and *vv* is less than that of *w*, *i* and *l*, the gas takes the direction *m*, *vv*, *p*, *rr*, and issues into the condenser G. The tube *p* is usually fixed in such a position that the slightest displacement is sufficient to cause the gas to pass in either direction. During the evolution of the gas and saturation of the liquids, the equilibrium between the free and absorbed gases and the complete expulsion of the air, is effected by allowing the gas to pass through the apparatus in both directions. The apparatus being thus filled with the sensitive gas, and the stopcock *h* shut, the observations are made by measuring the diminution of the volume of enclosed gas on the scale of the horizontal tube *ss* of accurately determined capacity.

It being necessary, as we shall hereafter show, in order completely to saturate the 10 or 12 grammes of water contained in the whole apparatus, to evolve not less than from 6 to 10 litres of the electrolytic gas, we found that the platinum wires in the evolution-tube were so quickly acted upon by the chlorine, that they had to be renewed after two or three days' use. This continual reparation of the apparatus was the more inconvenient, because, in the original saturation of the water, the gas has to be led through the apparatus for a period of from three to six days. After many fruitless attempts, we have at last overcome this difficulty by the following arrangement of the carbon-poles. Small carbon points or plates are cut off from the cylinder of a carbon-zinc element which has been long in use, and after they have been boiled in aqua regia, they are heated to whiteness in a stream of dry chlorine until all sublimation of chloride of iron or other volatile chlorine compounds has completely ceased. Platinum wires, whose ends have been sharpened and hardened by hammering, are then firmly fixed into small holes bored in the carbon-poles by a needle, and over the platinum wire is placed a thread of glass drawn out before the blowpipe. This thread is melted in the blowpipe flame at the point at which it touches the carbon, and pressed down over the carbon and wire so as to form a button of glass, as is seen in fig. 3, Plate XVIII. The whole wire and glass thread is then slowly drawn through the flame, so that the glass is completely melted upon the platinum wire, forming an enamel throughout its whole length, and completely protecting it from the action of the chlorine. In order to preserve the ends of the wires which are fixed into the carbon, from the action of the acid, it is sufficient to impregnate the upper end of the carbons with a little white wax. If the precaution be adopted of fusing the wires into the upper end of the tube, as is seen in fig. 2, so that the necessarily unprotected part of the wire does not come in contact with the liquid, no destruction of the electrodes, or of the wires need be feared, even when the instrument is in continual use. Another very important precaution which must be attended to regarding the electrodes, is that the carbon-poles must never be allowed to come in contact with the free gas, for carbon prepared in the manner described, acts upon the mixture of chlorine and hydrogen exactly as spongy platinum acts upon the mixture of oxygen and hydrogen. In the course of our experiments we have had many opportunities of observing this catalytic action of the carbon, and more than once has this action proceeded so rapidly that inflammation of the gaseous mixture has occurred, and the apparatus was shattered with a sharp explosion.

The varying stand of the water in the horizontal tube *ss* can be conveniently observed by the light of a distant candle or lamp, which exerts no perceptible action on the sensitive gas.

The following conditions, necessary in order to obtain exact photo-chemical measurements with a mixture of chlorine and hydrogen, are completely fulfilled in the apparatus just described.

(1) The gas which is exposed to the action of the light consists of exactly equal volumes of chlorine and hydrogen.

(2) It does not contain any foreign impurities.

(3) Throughout the whole apparatus it does not come in contact with caoutchouc or other organic matter which could alter its composition.

(4) The change of pressure during the whole series of observations is quite imperceptible, owing to the volume of water in the vessel *l* being much larger than that in the observation-tube *ss*.

(5) The statical equilibrium between the absorbed and free gases can be perfectly established.

(6) The layer of water in the insolation-vessel *i* does not alter its position during the experiment, so that the hydrochloric acid formed by the action of the light is always absorbed under precisely the same conditions.

(7) The vessel *i* is covered outside with black varnish, reaching as high as the level of

the water, so that no alteration in the free gas can ensue from the combination of the chlorine and hydrogen dissolved in the water.

(8) The volume of uninsolated gas which enters the vessel *i* from the horizontal tube *ss* during the observations, is very small compared with the total volume of gas exposed to the light. In most of the experiments it amounted to about $\frac{1}{5000}$ of the total volume for every division on the observation-tube.

(9) The disturbing action of radiant heat is fully eliminated.

Having thus explained the arrangement of our instrument, we now pass to a description of the experiments instituted for the purpose of testing its efficacy.

The first action of light on the electrolytic chlorine and hydrogen is accompanied by a phenomenon of a very peculiar nature, which we have named Photo-chemical Induction, to the full consideration of which a special section of this investigation has been devoted. On exposing the sensitive gas to a constant source of light, the chemical action does not at once commence to its full extent; to begin with, it is either not perceptible or of very slight amount, but gradually increases until a permanent maximum has been reached. The following experiment shows this gradual increase of the original action.

Series of Experiments III.

Time in minutes.	Corrected observation.	Action every minute.
0	100·0	
1	100·5	0·5
2	102·1	1·6
3	102·6	0·5
4	103·2	0·6
5	105·3	2·1
6	119·9	14·6
7	139·1	29·2
8	170·2	31·1
9	200·6	30·4

In the first minute the action was only 0·5, and after the lapse of eight minutes it had reached 31·1, at which it remained constant. The enlargement of the combining power of chlorine and hydrogen is also observed, when the amount of light falling on the gas is suddenly increased. This peculiar action of the light determines the method which must be followed in the measurement of the chemical rays. The observations can never be made use of until the successive differences have become constant. In order to form an estimate of the trustworthiness of an experiment from the regularity of the differences, and to eliminate as much as possible the slight variations in the working of the instrument, it is almost always sufficient to read off the stand of the liquid every minute, and to take the mean of ten or twelve such observations. The following experiment, calculated in this manner, gave the mean values as below:—

Series of Experiments IV.

Time.	Corrected observation.	Action of the light in one minute.	Mean action from three observations.
0	102·1		
1	104·2	2·1	
2	107·3	3·1	
3	113·5	6·2	
4	125·0	11·5	
5	135·4	10·4	
6	145·9	10·5	
7	159·3	13·4	
8	172·5	13·2	13·23
9	185·6	13·1	
10	198·8	13·2	
11	211·9	13·1	13·50
12	226·1	14·2	
13	237·2	11·1	
14	251·4	14·2	13·35
15	266·1	14·7	

The mean of the three values in the fourth column is 13·36, giving the following differences:—

Found.	Mean.	Difference.
13·23	13·36	+0·13
13·50	13·36	−0·14
13·35	13·36	+0·01

From these numbers, it is seen that by the combination of such a series of observations, the small irregularities, arising chiefly from capillary resistance in the tube *ss*, are satisfactorily eliminated.

In order to ascertain the limits of accuracy to which the indications of our instrument reached, it was necessary to determine, first, the length of time during which the electrolysis of a given volume of hydrochloric acid yields a gas of uniform composition; and secondly, the circumstances which influence the establishment of the statical equilibrium between the free and absorbed gases in the liquids contained in the apparatus. For this purpose we required a source of light which should remain constant for a considerable length of time; this we obtained by employing a coal-gas flame of constant dimensions issuing from SCOTT'S annular burner. A millimetre scale was etched upon the glass chimney of the lamp by hydrofluoric acid, and in order to avoid the errors arising from parallax, the height of the flame was read off on the scale through a telescope placed at the same height.

The amount of the chemical rays emitted by any flame depends upon its dimensions and its luminous intensity. We eliminated all sources of error arising from variations in the dimensions of the flame, by cutting off the greater part of the light with a screen, and thus employing only a small portion of the most intensely luminous rays as the source of light. In order that the intensity of the flame should remain as much as possible constant during our experiments, we determined the height of the flame of the

SCOTT'S burner at which an alteration in the dimensions of the flame produced the least variation in the luminous intensity. In the following experiments, conducted for this purpose, the intensity of the light from the most luminous parts of flames of different dimensions was measured by allowing the various amounts of light to fall through the same opening upon the sensitive gas in the instrument. The first horizontal division in the following Table contains the heights of the various flames measured by the millimetre scale on the chimney; the remaining divisions give the amount of chemical action produced by radiation from equal surfaces of the various flames.

Series of Experiments V.

Height of the flame.	82 millims.	95 millims.	110 millims.	133 millims.
Observed intensity of the chemical rays	21·0 22·0 19·0 21·0	18·77 19·17 17·61 19·23	15·84 17·51 16·59 17·20	9·0 9·0 9·0 9·0
Mean intensity	20·75	18·69	16·78	9·0

These experiments give the following variation in the intensity of the chemical rays for alteration in the heights of different-sized flames:—

Height of flame.	Intensity of chemical rays.	Difference of height.	Difference of intensity.
130 mm.	9·00		
		20·0 mm.	7·78
110 ,,	16·78		
		15·0 ,,	1·91
95 ,,	18·69		
		13·0 ,,	2·06
82 ,,	20·75		

Hence it is seen that when the flame is from 95 to 110 millims. in height, alterations in the size of the luminous cone are accompanied by the smallest alterations in the intensity of the chemical rays. For this reason, in all the experiments in which the annular burner was employed, we placed the flame at a height of about 100 millimetres. As the limit of height within which the flame could be kept constant was about 6 millimetres, and as according to the above experiments a variation of 15 millims. in the height of the flame causes an alteration of $\frac{1}{10}$ of the total intensity, the errors in the determinations arising from variations in the size of the flame could not amount to more than 4 per cent., supposing that no other errors occurred from differences in the composition of the coal-gas employed. The accurate agreement of a large number of photochemical measurements made at different times with the Heidelberg coal-gas, for the preparation of which the process remained unaltered during the period of our experiments, proved, as we shall show, that no appreciable difference in the intensity of the chemical rays occurred in the flame of coal-gas prepared at various times. The next point to determine was the influence which the strength of the electrolysed hydrochloric acid, as well as the intensity of the current employed to decompose it, exerted upon the composition of the sensitive gas; and the length of time which is necessary to lead the gas through the apparatus before all the air is expelled, and the requisite equilibrium between the absorbed and free gases established.

In order to answer these questions, we led a current of gas for several days through our instrument, freshly filled, observing from time to time the amount of action effected by the constant source of light. We obtained the following results, which were similarly observed each time the apparatus was refilled.

Series of Experiments VI.

Experiment 1.				Experiment 2.			
Duration of the saturation.	Action for each minute from twelve observations.	Duration of the saturation.	Action for each minute from twelve observations.	Duration of the saturation.	Action for one minute from twelve observations.	Duration of the saturation.	Action for one minute from twelve observations.
First day.		Fourth day.		First day.		Third day.	
h m		h m		h m		m	
1 9	0·00	30	9·65	1 5	0·00	5	9·90
15	2·49	1 1	18·39	1 35	0·00	10	10·10
15	3·06	15	23·06	33	2·08	30	11·52
Third day.		5	22·26	5	2·08	15	12·83
18	5·57	27	23·22	Second day.		20	12·92
16	5·21	10	25·63	30	5·93	15	13·64
25	5·36	1 8	19·66	20	6·41	10	13·60
39	5·01	15	17·28	15	7·40		
31	4·86	1 8	14·60	1 0	8·43		
39	5·14	Fifth day.		10	8·39		
1 19	3·32	15	26·49	35	6·60		
19	2·47	2	25·32				
29	2·12	2	27·19				
20	2·43	2	26·95				
		2	26·08				
		2	25·87				
		2	27·43				

From the first of these experiments, in which, as in all the later ones, hydrochloric acid of spec. grav. 1·148 was used, it is seen that after the gas had passed one hour through the apparatus the action was 0·0; after two hours' saturation the action rose to 5·57, at which amount it remained stationary after the gas had again passed through for 2½ hours; on further saturation the action diminished to about 2·43. The difference between the weight of the decomposing cell before and after the experiment, showed that 3755 cub. cent. of the chlorine and hydrogen mixture had passed through the vessel *i*, of about 7 cub. cent. capacity and containing 1·8 cub. cent. of water, and that the quantity of hydrochloric acid contained in the electrolyte had diminished from 30 to 20·5 per cent.

The experiment, which thus far had occupied two days, was extended over the following days, the diluted acid being replaced by concentrated acid. After the gas had passed through the instrument for half an hour the action increased to 9·65, and after saturation for another quarter of an hour the action amounted to 23·06, at which number it remained constant for several successive hours. On further saturation the action diminished to 14·6. The volume of gas which had passed through the insolation-vessel amounted to 2544 cub. cent., and the quantity of anhydrous acid contained in the electrolytic liquid had decreased from 30 to 21·4 per cent. On continuing the experiment on the fifth day with fresh hydrochloric acid, the action attained a maximum of 26·49 after the gas had been led through for fifteen minutes. This maximum action remained constant in all subsequent experiments with renewed quantities of acid, and in each case a short saturation sufficed to bring the gas to the maximum degree of sensibility, in which the action was 26·49.

The second series of experiments gives, as may be seen, the same general results as the one just described.

From these and a large number of similar experiments which we have made in the course of the testing of the instrument, the following conclusions may be drawn:—

(1) When the quantity of hydrochloric acid contained in the liquid electrolyte has decreased from 30 to about 23 per cent., the evolved gases are no longer fitted for comparative photo-chemical measurements.

(2) In order to attain the first constant action, at least 2000 cub. cent. of gas must be passed through the small vessel of 7 cub. cent. capacity, containing 1·8 cub. cent. of water.

(3) By continued saturation the action increases up to a certain point at which a permanently constant maximum is reached, which in our apparatus was not attained until more than 6000 cub. cent. of the chlorine and hydrogen mixture had passed through the insolation-vessel.

(4) The attainment of the necessary equilibrium in the apparatus is much accelerated by allowing the water to remain in contact with the gases during the night. Were the saturation continued without intermission, a much larger quantity of gas would have to be led through the apparatus before the maximum action is attained, than was required in the foregoing experiments. All the attempts which we have as yet made to shorten this most tedious period of preparation necessary for the execution of photo-chemical measurements with chlorine and hydrogen have proved fruitless.

Long experience has shown that the apparatus is most conveniently filled by the following manipulation. The operation is commenced in the morning by filling the evolution-tube *a*, fig. 2, with about 55 cub. cent. of hydrochloric acid of spec. grav. 1·148, and leading through the apparatus the gas evolved from this cell at such a rate that about two bubbles pass through the washing-bulbs and insolation-vessel every second of time. In the afternoon, the acid, which can be reduced by 7 per cent. of its original volume, is changed, and the operation repeated, with the important exception that the gas evolved during the first hour, containing air and excess of hydrogen, is not allowed to pass through the apparatus, but escapes through the manometer by the tubes *m*, *vv*, *p* into the condenser G. The instrument, protected from all exposure to light, is then allowed to stand during the night with the stopcock closed, and the operations are commenced in the morning anew, care being always taken to allow the impure gas to escape during the first hour of evolution. During the intervals of saturation, the photo-chemical sensibility of the gaseous mixture is determined by observing the action produced by a gas-flame of constant dimensions.

As soon as a maximum action has been reached, which generally occurs in from three to six, sometimes even from eight to nine days, according to circumstances, the instrument can be used for comparative measurements extending over a period of several months, and requires only a short preparation to enable it to give correct results throughout the day. All that is necessary for this purpose, is to pass the gas evolved from fresh hydrochloric acid, for an hour through the manometer *m*, and afterwards the glass stopcock *h* is opened, and the gas allowed to pass through the apparatus for from fifteen minutes to an hour, after which the maximum action has generally been attained. As soon as the stopcock is shut, in order that the observations may be begun, the balance-wire of the gyrotrope is reversed, so that the hydrochloric acid is constantly decomposed by a very feeble current. If this precaution be neglected, the equilibrium of the gases dissolved in the acid is soon destroyed, owing to a contact-combination of the chlorine and hydrogen taking place on the surfaces of the carbon-poles. Above all, access of air in the washing-bulbs and in the insolation-vessel must be most carefully avoided. If the insolation-vessel be removed from the apparatus for merely a few moments, a saturation lasting from two to six days is necessary before the maximum degree of sensibility is again reached. The amount of foreign gas which is sufficient to render the indications of the instrument incorrect, cannot approach to a billionth part of the total volume of gas. We shall have occasion to return to this remarkable fact in a later part of the research; but we may here remark, that when the maximum action has been reached, the explosive nature of the gas is so great, that a thin glass bulb of the size of a pigeon's egg filled with the gas, immediately explodes on exposure to the diffuse light of an overclouded sky at an open window. On taking the apparatus to pieces, portions of the gas have several times exploded on exposure to evening light, even after the sun had disappeared below the horizon.

Having thus determined the conditions which must be fulfilled in order to obtain comparative results, we proceed to the examination of the influence which the heat radiated from the source of light, and the heat of combustion evolved by the combination of the gases, exert upon the indications of the instrument.

The relation between the volumes of the insolation-vessel used in these experiments, and the volume occupied by one division on the observation-tube, was as 7430 to 1. Hence, if this vessel were heated from 0° C. to 0°·0366 C., the whole mass of gas would be increased by a volume represented by one division of the tube. Our instrument is therefore not only a photometer, but also a very sensitive air-thermometer, and all experiments with it must be conducted in a space within which the changes of temperature are not large enough to cause any perceptible error.

This condition was fulfilled by experimenting in a room of which the outer wall was at no time of day exposed to the direct sunlight, and the only window completely closed from without.

In order to eliminate the more serious errors arising from the radiant heat of the source of light, we placed, as we previously mentioned, a glass cylinder, N, Plate XVII. fig. 2, closed by plates of glass and filled with water, between the source of light and the insolation-vessel *i*. In addition to this water-cylinder, the insolation-vessel was further protected from access of radiant heat by the double metallic screen, fig. 4, placed between the insolation-vessel and the water-cylinder N, fig. 2. The apertures in the middle of each sheet of metal were closed by perfectly clear thin plates of mica, behind which was placed the insolation-vessel *i* contained in the blackened cap *c* and covered by the lid *d*. Lateral slits in the cap, with others corresponding in the lid, allowed the tubes *oo* to pass out, and currents of air were excluded by stopping the lateral slits with black wool. As it is important to observe the height of the flame whilst the absorption is being read off on the scale, a small hole, *l*, was made in the lid *d*, through which the point of the flame could be easily seen.

By this arrangement all errors arising from radiant heat were completely excluded, for it was found that if the vessel *i* were filled with a gas which is not sensitive to light, the stand of the water in the observation-tube remained constant, whether the gas were exposed to the light or not.

It now only remained to determine the effect produced on the indications by the heat evolved from the combination of the gases. A phenomenon of great importance here presented itself. If the insolation-vessel be suddenly darkened during the normal working of the apparatus, it is found that the action does not instantly cease, but that the volume s_0 of gas read off at the moment of darkening t_0 diminishes after the lapse of the times $t_1t_2\ldots t_n$ to the volumes $s_1s_2\ldots s_n$, so that for the times $(t_1-t_0)(t_2-t_1)$, &c., after the light had been cut off, a corresponding decrease of volume $(s_0-s_1)(s_1-s_2)$ is found. The time during which this decrease of volume takes place is a very short one, as may be seen from the following experiments, made at 20°·9 C. and 0^{m}·7497 Barom.

Series of Experiments VII.

Experiment 1.					Experiment 2.					Experiment 3.				
	Time in seconds. *t*.	Observations on the scale.* *s*.	t_1-t_0.	s_0-s_1.		Time in seconds. *t*.	Observations on the scale. *s*.	t_1-t_0.	s_0-s_1.		Time in seconds. *t*.	Observations on the scale. *s*.	t_1-t_0.	s_0-s_1.
	″		″			″		″			″		″	
Insolated	0	241·0	60	12·5	Insolated	0	293·5	60	14·0	Insolated	0	339·5	30	17·5
	60	253·5	60	12·0		60	307·5	60	14·0		30	322·0	30	16·0
	120	265·5	60	12·5		120	321·5	10	1·5	Darkened	60	306·0	30	5·0
Darkened	180	278·0	10	1·5	Darkened	130	323·0	10	0·3		90	301·0	30	1·0
	190	279·5	10	0·2		140	323·3	10	0·1		120	300·0	30	0·0
	200	279·7	10	0·1		150	323·4	10	0·0		150	300·0		
	210	279·8	10	0·0		160	323·4	10	0·0					
	220	279·8	10	0·0		170	323·4							
	230	.279·8	10	0·0										
	240	279·8												

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* The increasing numbers on the divided arbitrary scale of the instrument correspond to a diminution of the volume of the total gas.

Experiment 1 shows that in the first 10″ after the withdrawal of light, the volume of gas diminished 1·5 volume, in the following 10″ 0·2, in the next 10″ 0·1 volume, and that then no further diminution was perceptible. In experiment 2 the diminution of volume amounted in the first 10″ to 1·5, in the following 10″ to 0·3 volume, and in the next 10″ to 0·1 volume, after which the gas preserved its constant volume. In experiment 3 the volume diminished after the first 30″ by 5·0 volume, after the second 30″ by 1·0 volume, and then the water in the tube remained stationary. This subsequent action, after removal of light, may arise from several causes.

In the first place, the slow combustion of the chlorine and hydrogen produces a known amount of heat, and the increased degree of temperature W_0, arising therefrom, becomes constant when the amount of heat lost by radiation and conduction is equal to the amount added by combustion of the gases. The gas in the insolation-vessel is therefore always warmer than the surrounding medium by a temperature (W_0-W_n) where W_n represents that of the air. When the insolation, and with it the supply of heat, ceases, the gas cools down from W_0 to W_n, and the contraction ensuing from this diminution of temperature accounts for at least a portion of the action observed after withdrawal of the light. This subsequent contraction may, in the second place, be caused by the non-instantaneous absorption, by the water, of the hydrochloric acid formed by the slow combustion of the chlorine and hydrogen. In this case, as with the heat, an equilibrium between the amount of hydrochloric acid formed and that absorbed by the water, will ensue as soon as the quantity of acid absorbed is equal to that produced, and a constant amount of hydrochloric acid will remain in the gaseous mixture. With the exclusion of light the supply of hydrochloric acid ceases, and this constant amount of acid is absorbed by the water, causing a corresponding diminution in the volume of the gaseous mixture. Lastly, it is possible that the combination of the chlorine and hydrogen does not instantly cease with the exclusion of light, but that by insolation the gases are brought into a condition of increased affinity, which continues for a certain time in the dark. As these three conditions might exert a great influence upon the action of our instrument, we thought it necessary to determine their relative importance.

The three questions to be solved were,—

1st. What is the influence exerted by the slow combustion of the chlorine and hydrogen upon the action of the instrument?

2ndly. To what extent can the hydrochloric acid formed by insolation, but not absorbed by the water, cause an irregularity in the indications?

3rdly. Is the presence of light necessary for the combination of the chlorine and hydrogen, or can this combination occur for a short time after exclusion of light?

The following considerations prepare the way for the solution of these questions.

When a sensitive mixture of chlorine and hydrogen is exposed to the action of light, the temperature of the gas gradually rises up to a point at which it remains stationary, owing to the amount of heat absorbed being equal to that evolved from the combustion of the gases. As the amount of heat evolved by the combination of the chlorine can be calculated from experiment, we only require to determine the amount of heat absorbed during the same space of time in order to obtain the value of (W_0-W_n), or the difference of temperature between the gas and the surrounding medium. If the volume of gas burnt in the unit of time immediately before exclusion of light, measured in cubic centimetres at the temperature W_0 and pressure P, be called R, the weight in grammes of the chlorine combined with hydrogen in the unit of time is found from the formula

$$\frac{s_1}{773} \cdot \frac{P}{0{\cdot}76\,(1+0{\cdot}00366\,W_0)}\,\frac{R}{2}=A,$$

where s_1 is the specific gravity of chlorine. If, therefore, the amount of heat evolved by the combustion of 1 grm. of chlorine with hydrogen, measured by the rise of temperature of 1 grm. of water, be called C, the amount of heat evolved from combustion of the chlorine in a unit of time expressed in units of heat is AC.

The quantity of heat absorbed can be calculated when the cooling-velocity of the insolation-vessel for a degree Centigrade is known. In order to determine this value, which we may call a, we exchanged our insolation-vessel for another of the same dimensions, in the interior of which a fine platinum wire was fixed by fusion through the glass. When a weak current of electricity was passed through the wire, the sensitive gas being protected from the action of the light, an immediate expansion by heat occurred, which, as soon as the current was interrupted, gave place to a corresponding contraction. As the weight of the insolation-vessel was at least 1000 times greater than that of the gas contained in it, the amount of heat communicated from the gas to the vessel may be regarded as infinitely small.

The observations for the determination of a were thus conducted. First, the constant position w_n of the water in the tube was noted; then, after the gas had been expanded to the position w_0 by means of the current passing through the platinum wire, the electricity was cut off and the time observed, by means of a pendulum vibrating half seconds, during which the gas diminished in volume from w_0 to w_1. According to this method of observation, it was only necessary to determine the interval of time during which the volume of gas diminished a constant amount; hence results of sufficient accuracy were obtained, notwithstanding the rapidity at which the gas cooled down.

The determination gave the following numbers:—

Series of Experiments VIII.

	Exp. 1.	Exp. 2.	Exp. 3.	Exp. 4.	Exp. 5.
w_0	320	355	427	420	427
w_1	310	340	420	410	420
w_n	300	330	410	400	410
Time t_0-t_1 in which the change w_0-w_1 occurred	$1''{\cdot}1$	$0''{\cdot}9$	$1''{\cdot}1$	$1''{\cdot}2$	$1''{\cdot}1$

The figures in the first three horizontal divisions may be supposed to represent temperatures measured on a relative but arbitrary scale.

The excess of temperature of the gas over that of the surrounding medium was therefore, for the time $t_0\, t_1 \ldots$, $w_0 - w_n = u_0$, $w_1 - w_n = u_1 \ldots$; and if a represents the cooling velocity for the thermometric unit and this difference of temperature, we have

$$\frac{du}{dt} = -au.$$

The integral of this differential equation is $\log \text{nat}\, u = -at + \text{const.}$, and according to definition of u_0, u_1, t_0 and t_1, $\log \text{nat}\, u_0 = -at_0 + \text{const.}$, and $\log \text{nat}\, u_1 = -at_1 + \text{const.}$ Hence

$$a = \frac{\log \text{nat}\, u_0 - \log \text{nat}\, u_1}{t_1 - t_0}.$$

The values of a, calculated from the experiments according to this formula, are as follow:

	a.	Difference.
Exp. 1 . . .	0·630	−0·047
Exp. 2 . . .	0·567	−0·110
Exp. 3 . . .	0·806	+0·129
Exp. 4 . . .	0·578	−0·099
Exp. 5 . . .	0·806	+0·129
Mean . .	0·677	

Although the difference between each value of a and the mean is considerable, yet in the calculation of the temperature this variation has very little influence, a difference of 0·11 in the value of a causing an error of only a few hundredths of a centesimal degree.

If the difference of temperature between the gas and the surrounding medium at the moment of exclusion of light is $(W_0 - W_n)$, measured in centesimal degrees, the cooling-velocity immediately after darkening is $a\,(W_0 - W_n)$. If, further, the volume in cub. cent. of the gaseous mixture at the moment of closing is called V_0, its specific gravity s, the pressure to which it is subject P, its temperature W_0, and its specific heat by constant pressure compared with water c; and if the weight of the platinum in the vessel is p, and its specific heat c_1, the decrease of temperature in the unit of time during the cooling, expressed in units of heat representing the amount required to raise one cub. cent. of water one degree Centigrade, is found from the expression

$$\left\{\frac{P}{0{\cdot}76\,(1+0{\cdot}00366\, W_0)} \cdot \frac{sc}{773}\, V_0 + c_1 p\right\} a\,(W_0 - W_n).$$

As the amount of heat evolved by combustion is equal to that lost by radiation, we have

$$\frac{s_1}{773} \cdot \frac{P}{0{\cdot}76\,(1+0{\cdot}00366\, W_0)}\, \frac{RC}{2} = \left\{\frac{sc}{773} \cdot \frac{P}{0{\cdot}76\,(1+0{\cdot}00366\, W_0)}\, V_0 + c_1 p\right\} a\,(W_0 - W_n).$$

As the values of W_0 and W_n differ only by a few hundredths of a degree Centigrade, it is possible to replace the value $(1+0{\cdot}00366\, W_n)$ for $(1+0{\cdot}00366\, W_0)$ without exceeding the limits of the errors of observation. Hence if $A = \frac{s_1 PC}{2.773.0{\cdot}76\,(1+0{\cdot}00366\, W_n)}$, and $B = \frac{scP}{773\,.\,0{\cdot}76\,(1+0{\cdot}00366\, W_n)}$, we have

$$A.R=(B.V_0+c_1p)\,a\,(W_0-W_n)\text{; and hence}$$

$$W_0-W_n=\frac{A.R}{a\,(BV_0+c_1p)}.$$

In order to be able to employ the experiments communicated in Series VII., page 369, for the calculation of (W_0-W_n), the volumes read off on the divided scale were reduced to cub. cent., and placed in the following Tables:—

Series of Experiments IX.

Experiment 1.			Experiment 2.			Experiment 3.		
Time.	Volume in cub. cent.	Diminution of volume in one second.	Time.	Volume in cub. cent.	Diminution of volume in one second.	Time.	Volume in cub. cent.	Diminution of volume in one second.
Insolated 0′ 0″	4·20926	0·000157	Insolated 0′ 0″	4·20255	0·000176	Insolated 0′ 0″	4·20929	0·000423
1 0	4·19983	0·000151	1 0	4·19199	0·000176	0 30	4·19660	0·000402
2 0	4·19078	0·000157	Darkened 2 0	4·18143	0·000113	Darkened 1 0	4·18453	0·000126
Darkened 3 0	4·18136	0·000113	2 10	4·18030	0·000022	1 30	4·18075	0·000025
3 10	4·18023	0·000015	2 20	4·18008	0·000008	2 0	4·18000	0·000000
3 20	4·18008	0·000008	2 30	4·18000	0·000000	2 30	4·18000	
3 30	4·18000	0·000000	2 40	4·18000	0·000000			
3 40	4·18000	0·000000	2 50	4·18000				
3 50	4·18000							

The constants required for this calculation are,—

$s_1=2·4531$ $\qquad a = 0·677$

$s=1·2612$ $\qquad C=669·9$

$c_1=0·0324$ $\qquad P = 0·7497$

$c=0·2114$ $\qquad W_n=20°·9$ C.

$p=0·0120$

The values of A and B, and from these (W_0-W_n), calculated from these data, are found in the following Table, in which the variables V_0 and R are placed in the first and second horizontal divisions:—

	Exp. 1.	Exp. 2.	Exp. 3.
V_0	4·18136	4·18146	4·1845
R..............	0·000157	0·000155	0·0004128
A	0·96859	0·96859	0·96859
B..............	0·0003144	0·0003144	0·0003144
(W_0-W_n)...	0°·13	0°·13	0°·35

These results prove that the photo-chemical combustion of the chlorine and hydrogen mixture may be increased from 12 or 14 divisions in the minute up to 32 or 35, whilst the increase of temperature accompanying this increased action amounts only to 0°·2 C. As various later experiments have shown that differences of several degrees in temperature do not affect the combining power of the chlorine and hydrogen mixture to any appreciable extent, we may answer the first question as follows:—

(1) That the heat evolved in the insolation-vessel from the photo-chemical combustion of the chlorine and hydrogen exerts no perceptible influence upon the combining power of these gases, or on the indications of our instrument; and

(2) That in the first few seconds after a change from one amount of light to another, irregularities in the indications of the instrument will be observed, but that these irregularities do not extend over a period longer than a few seconds, after which time a constant temperature in the insolation-vessel is attained.

Having thus calculated from the heat of combustion and from the cooling-velocity, the constant temperature which the gaseous mixture attains by exposure to various amounts of light, it is easy to solve the two other questions stated at the commencement of the inquiry. From the preceding considerations we have determined the value of (W_0-W_n), or the excess of temperature of the gas above the surrounding medium. Hence the decrease of volume Δ, which the gas suffers in cooling from W_0 to W_n, is known. If this calculated decrease of volume Δ is equal to that actually observed, Δ_1, the whole of the phenomenon is explained by the contraction from diminution of temperature. If, however, the calculated decrease Δ is not so large as the observed decrease Δ_1, a certain diminution of volume $\Delta_1-\Delta$ must be caused by absorption of the hydrochloric acid, or by a chemical action taking place after removal of light. From the following Table, in which the observed and calculated contractions are expressed as per-centage of the total volume, it is seen that the first supposition is the true one, as the values of $\Delta_1-\Delta$ are extremely small, and all negative.

	Δ_1.	Δ.	$\Delta_1-\Delta$.
Exp. 1.........	0·033	0·042	−0·009
Exp. 2.........	0·034	0·042	−0·008
Exp. 3.........	0·108	0·119	−0·011

Hence we may conclude,—

(1) That the amount of hydrochloric acid formed during the insolation is absorbed almost as quickly as it is produced, and therefore the insolated gas can contain only a trace of this substance; and

(2) That the chemical action ceases instantly on exclusion of the light, proving the absence of any perceptible amount of after-action.

* * *

The light emitted from a SCOTT'S annular burner, although it gives, as we have shown, satisfactory results, and may serve for many photometric observations, is, however, not sufficiently constant to serve for more accurate measurements. We therefore endeavoured to find means to obtain a flame of coal-gas of constant dimensions and luminous intensity.

Flames of coal-gas issuing under the usual pressure of several lines of water, and burning free in the air, vary and flicker far too much to allow them to be made use of for photo-chemical measurements. These variations of the flame can be best prevented by allowing the gas to issue from a small air-chamber, and by surrounding the flame with a screen so that all lateral currents of air are completely excluded.

We have found that by means of the arrangement represented in Plate XVIII. fig. 5, a flame of coal gas could be obtained of extremely constant dimensions and luminous power. AA_1, fig. 5, is a blackened tin box in the interior of which the gas-flame *l* burns. The bottom of the box is perforated to admit of an upward current of air, and the sliding front of the box is furnished with a screen of water, *a*, contained between two parallel plates of glass. The gas streams from the delivery-tube *b* into the small air-chamber *c*, and issues from the platinum burner with a pressure of about 1 millim. of water, as is seen by the small manometer *g* attached to the air-chamber. The dimensions of the flame are kept constant by regulating the supply of gas, so that the highest point of the flame always touches the thin platinum wire attached to a moveable ring fitting on to the divided tube *h*, upon which the height of the flame can be read off. In order to place the flame at any wished-for distance from the insolation-vessel, the tube *b* carrying the gas-burner can be moved through a holder, *k*, at the back of the box, and the distance read off on an etched millimetre scale. When the distance of the insolation-vessel from the flame has been once measured for a known position of the flame, a simple observation on the divided tube *b* gives the required distance. When the box was in use the top was covered on each side of the flame, leaving only a space of about two inches open. The dimensions of the flame burning in the box thus adjusted, when observed through the opening of the screen, *l*, fig. 4, were seen to remain perfectly constant, so much so that the light appeared to be emitted from a solid body.

We have employed this flame, which for the sake of brevity we shall call the standard flame, in the first place for the purpose of determining the constancy of the indications of the instrument at different times and under various circumstances. For this purpose, the chemical intensity of the light proceeding from standard gas-flames of the same heights was repeatedly measured at various intervals during sixteen days in the month of June 1856. In all these measurements, each one of which is the mean of ten independent observations, the height of the standard flame was 42·2 millims., and the distance between the flame and insolation-vessel was 216·0 millims.

Series of Experiments X.

Time of the observations.	Action in one minute.	Deviation from mean value.
11th June ...	14·00	+0·01
12th „ ...	14·26	+0·35
13th „ ...	13·80	−0·11
19th „ ...	13·83	−0·08
21st „ ...	13·88	−0·03
26th „ ...	13·71	−0·19
Mean value ...	13·91	

In order more fully to test our instrument, we made, some time later, other determinations which are of interest in a different point of view. It is well known that supporters are still found for the idea that photo-chemical phenomena are not to be ascribed to the action of the common luminous rays of a particular refractive index, but to a peculiar agent differing entirely from light, and possibly subject to other laws. In order to free our investigations from any objections which might be made from this point of view, we have endeavoured to avoid as much as possible applying the general laws of light to the chemically active rays without previous experimental proof. On this account we thought it advisable, whilst testing the reliability of the instrument, to prove that the action of the chemical rays diminishes inversely as the square of the distance from the point from which the light emanates. These experiments were conducted by determining the amount of chemically active rays which fall upon the insolation-vessel from the standard flame placed at various known distances in the blackened box. The first vertical column of the following Table contains the distance between the standard flame and the middle point of the insolation-vessel; the second column the reciprocals of the squares of these distances; the third the chemical action, W, measured by the instrument; and the fourth the amount of action, W_1, calculated according to the distance by means of the formula

$$\frac{\Sigma W}{\Sigma \frac{1}{r^2}} \cdot \frac{1}{r^2} = W_1.$$

Series of Experiments XI.

Experiment 1.						Experiment 2.					
	r.	$\frac{1}{r^2}$.	W.	W_1.	Difference.		r.	$\frac{1}{r^2}$.	W.	W_1.	Difference.
1	0·3900	6·575	3·98	4·11	−0·13	1	0·3900	6·575	4·43	4·32	+0·11
2	0·3310	9·127	5·56	5·70	−0·14	2	0·3315	9·108	6·07	6·00	+0·07
3	0·2495	16·064	10·33	10·05	+0·28	3	0·2150	21·634	14·07	14·24	−0·17

In these last experiments the standard flame was adjusted at exactly the same height as was the case in Series X., when the distance from the flame to the insolation-vessel was $0^{m}\cdot 216 = r_1$. These series of determinations may therefore be compared with one another by means of the formula $W_0 = \frac{W r^2}{r_1^2}$, from which the following values are obtained for the corresponding action at the distance $0^{m}\cdot 216$, as employed in Series X.

(1) 14·44,
(2) 14·28,
(3) 14·11.

The last number agrees very nearly with the mean action 13·91 of Series X., the difference being scarcely larger than that found among the single determinations of Series X.

In order to have still more striking proof of the accuracy of the indications of our instrument, we have compared the results obtained from the standard flame of coal-gas in June with those of the same-sized flame in September, when all the liquids contained in the apparatus had been renewed. The standard flame, of the same size as previously employed, was placed at a distance of $0^{m}\cdot1365$ from the insolation-vessel, and the instrument was furnished with a new observation-tube, whose degrees were 3·40 times larger than that employed in Series X. An action of 10·17 degrees per minute was obtained as a mean of 96 well-agreeing observations: this 10·17, reduced to the former scale, represented 34·58 degrees, which gives for the distance $0^{m}\cdot216$ the action 13·80, which differs from the June mean 13·91 by only 0·11.

The exact agreement of these numbers at such distant periods of time is the more remarkable, as it could not have been expected that the coal-gas generated by a common manufacturing process should possess so constant a composition that it could be used during the space of several months as a fixed unit for the measurement of photo-chemical action. In order to form an idea in how far the intensity of the chemical rays emanating from a flame is dependent upon the composition of the gases undergoing combustion, it was necessary to determine the variation in the composition of the gas employed in the experiments.

Although we have not analysed the gas employed in each experiment, we are still able to give the composition of the gas employed by us from a series of analyses made for another purpose by Dr. LANDOLT at various times during the course of our investigations.

Four samples of Heidelberg coal-gas, collected by LANDOLT on the spot and at the time at which our experiments were conducted, gave, on analysis, the following results:—

	I.	II.	III.	IV.
Hydrogen	39·30	41·04	44·00	41·37
Light carburetted hydrogen.	40·56	40·71	38·40	38·30
Carbonic oxide	4·95	7·64	5·73	5·56
Elayl	4·04	5·10	4·13	5·00
Ditetryl	3·15	2·18	3·14	4·34
Nitrogen	8·00	2·75	4·23	5·43
Oxygen	0·00	0·00	0·00	0·00
Carbonic acid	0·00	0·58	0·37	0·00
	100·00	100·00	100·00	100·00

Hence it is seen that the composition of the Heidelberg coal-gas varies but little during a considerable period, but still sufficiently to render the exact agreement of the photo-chemical measurements very remarkable.

In order to determine which of the ingredients of the flame principally influences the amount of the chemically active rays, we have made the following experiments with a gas-lamp, which has been introduced by one of us into the laboratory to supersede the ordinary wire-gauze flame, and is particularly well suited to produce a flame of various degrees of luminosity and of varying form and colour. The principle upon which the lamp is constructed, is simply that the gas is allowed to issue under circumstances in which it mixes with such a quantity of air, that the mixture does not quite reach the point at which it is combustible without addition of oxygen. This condition is fulfilled by the following simple arrangement:—*a*, fig. 6 (Plate XVIII.), is a common triangular burner, rising inside the cylindrical cavity *b* to the surface of the cube *cc*. This cylindrical opening, *bb*, which is 15 millims. in depth and 10 millims. in diameter, communicates with the outer air by four holes, *dd*, 7 millims. in diameter. After screwing on the tube *e*, which is 76 millims. long and 8·5 millims. in diameter, the coal-gas is allowed to issue from the burner *a*. On issuing, the gas causes a current of air to enter the tube by the holes *dd*, and the mixture burns at the upper end of the tube with an almost colourless flame perfectly free from smoke. On closing the openings *dd*, the original luminous smoky flame of coal-gas appears.

In order to obtain a large and steady brightly-coloured flame, a small hollow cylinder of porous coke, saturated with a concentrated solution of the salt which colours the flame, is placed on the upper end of the tube *e*. These small cylinders of carbon are best prepared from the carbon employed as the negative pole in a zinc-carbon battery. In order to obtain the purest and brightest-coloured flame, it is necessary to be very careful to select pure salts, and to free the coke cylinder as much as possible from all foreign ingredients by ignition in a stream of chlorine, and boiling out in aqua-regia.

In the first place, the openings *dd* were closed, and the action of the luminous flame was found to be 21·5 in the minute. As soon as the holes *dd* were opened, and the illuminating power of the flame vanished, all perceptible chemical action also ceased. As the heat evolved in the non-luminous is greater than in the luminous flame, and as the two flames only differ by the one containing incandescent particles of carbon which are wanting in the other, we must conclude that the chemical action is chiefly effected by the rays proceeding from the incandescent carbon liberated during the combustion. This carbon is produced from the elayl and ditetryl, the first of which varied in the samples of gas analysed from 4 to 5 per cent., and the second from 2 to 4 per cent. The exact photo-chemical measurements made with different portions of this gas appear, therefore, to point out that the amount of carbon set free in the combustion of coal-gas depends rather upon the dimensions and form of the flame than upon the small variations in the composition of the gas. After the incandescent carbon, the carbonic oxide in the flame appears to effect the most chemical action, and although the small amount of 6 or 7 per cent. of carbonic oxide in the coal-gas is insufficient to cause any perceptible action, still the flame of pure carbonic oxide produces much more action than that of hydrogen or light carburetted hydrogen. The smallest trace of foreign bodies in the flame can exert a great influence on the chemical action. The red, violet, yellow and green flames produced by the chlorides of lithium, strontium, potassium, sodium and barium, which can be seen to great advantage by the arrangement just described, give no more chemical action than the colourless flame. The fine green flame produced by chloride of copper, and the pale flame produced by chloride of antimony are, on the contrary, so rich in chemically active rays, that the action begins as soon as the saturated coke is placed on the tube; and in one case it reached the amount of twenty-seven divisions in one minute.

At the end of this Part we have to consider the important question regarding the influence which the changes in atmospheric temperature exert on the indications of the instrument. For this purpose we have conducted four series of observations on the 17th, 18th, 19th, and 20th of September, 1856, in a room the temperature of which was kept constant within half a degree Celsius, during the filling and observation with the apparatus. The volume represented by one degree on the observation-tube was 3·4 times as large as in Series X. The distance between the flame, of the same height as in the former experiments, and the insolation-vessel was $0^{m}\cdot1365$. In order to compare the results thus obtained with those of Series X., it was only necessary to multiply the observations with the factor $\frac{3\cdot4\,.\,0\cdot1365^2}{0\cdot216^2}=0\cdot1358$.

The observed values are placed in the following Table. The first vertical column contains the constant temperatures at which the apparatus was filled and the observations made; the second, the action produced by the constant standard flame every minute, expressed in degrees of the instrument (a mean of eight actual observations); the third, the mean of these actions, and the fourth their differences.

Series of Experiments XII.

I.	II.	III.	IV.
18°·0 C.	14·24	14·39	
	14·54		+0·54
19·4	13·85	13·85	
	13·85		
25·8	14·23		−0·71
	14·73	14·56	
	14·73		+0·30
26·3	14·11	14·26	
	14·42		

From the irregularity of the signs of the differences in the fourth column, we may conclude that the indications of the instrument remain unaffected by changes of temperature between 18° C. and 27° C., any alteration which takes place falling within the limits of observational errors.

As the barometric pressure varied in the foregoing experiments from $0^{m}\cdot746$ to $0^{m}\cdot760$ without the differences between the indications becoming perceptibly larger, the influence of the changes in the atmospheric pressure can be overlooked, except in cases in which greater accuracy, as in the reduction to absolute measure, is required. In a later Part, when treating of the relation of the chemical action to the density of the chlorine and hydrogen mixture, we shall describe experiments in which the influence of the atmospheric pressure is corrected.

In the next Part we shall consider the relations of Photo-chemical Induction, under which term we class a number of phenomena which open a new and most interesting field of investigation, and are connected in an intimate manner with catalytic actions.

Fig. 1.

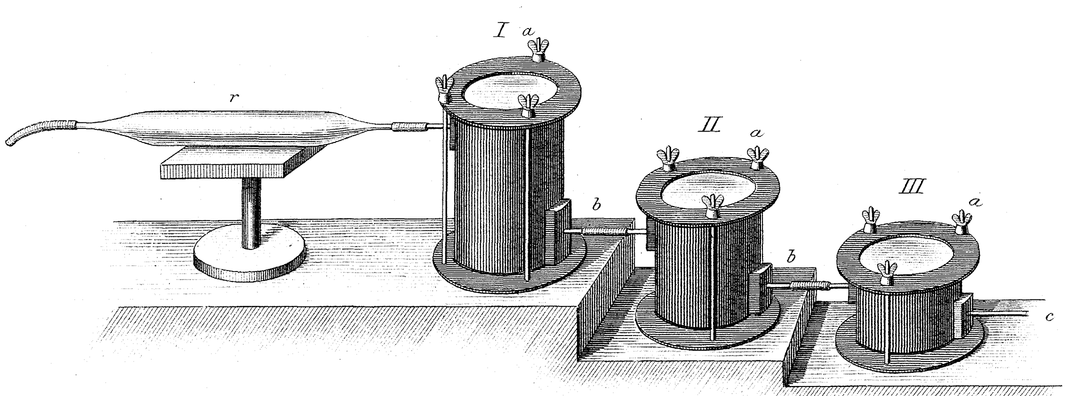

Fig. 2.

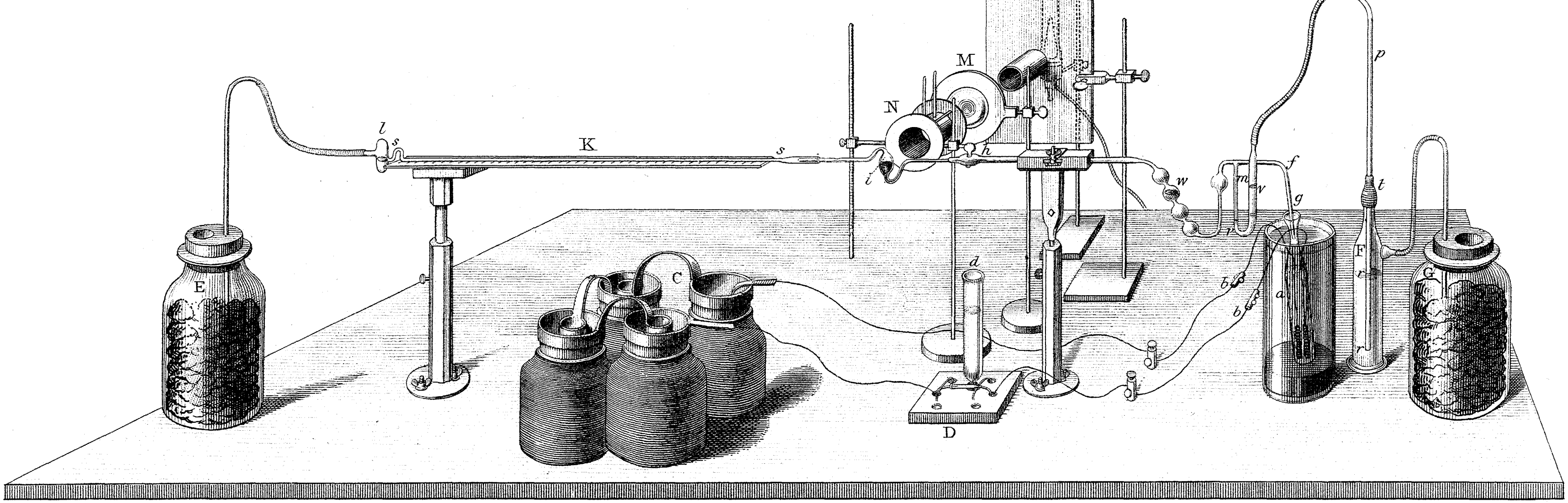

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Fig. 3.

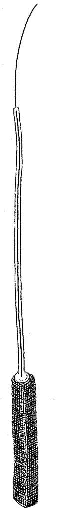


Fig. 4.

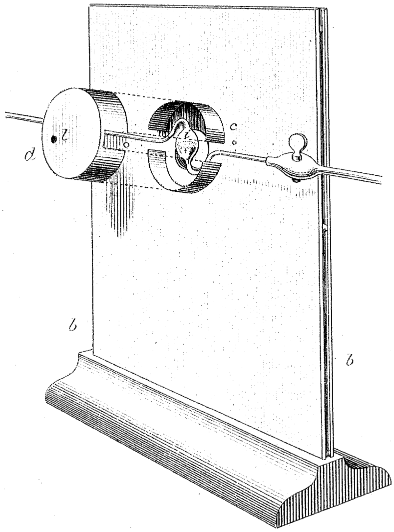


Fig. 5.

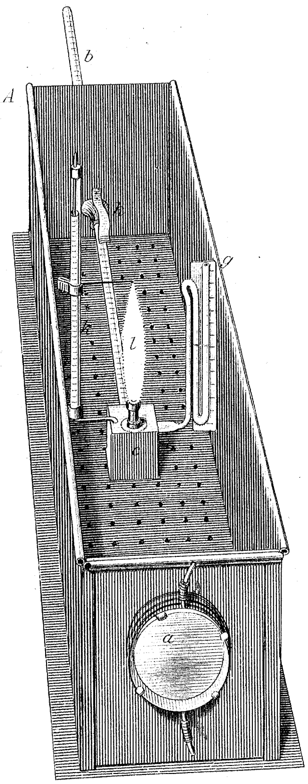
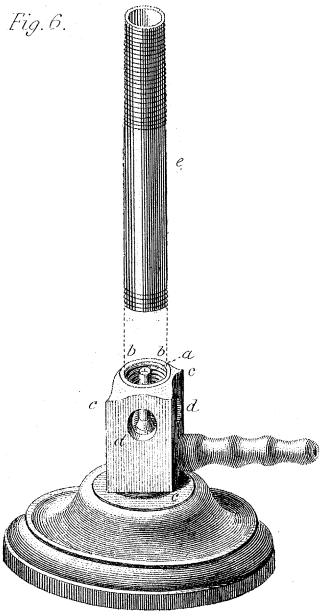


Fig. 6.



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