On Chemical Dynamics and Statics under the Influence of Light

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VI. *On Chemical Dynamics and Statics under the Influence of Light.*

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Introduction.

The nature of the forces which come into play when substances react one upon another chemically, is a problem which has specially engaged scientific minds during the last century. During the second half of that period chemical statics and dynamics have developed into a veritable science. The general law governing the velocity of chemical reaction and chemical equilibrium in homogeneous systems is now known as the law of mass action, and was to a great extent foreseen by Berthollet.* In heterogeneous systems the law concerning the velocity of physical

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* C. L. Berthollet, 'Essai de Statique Chimique,' 1803; Wilhelmy, 1850; Harcourt and Esson, 1866; Guldberg and Waage, 1867; van't Hoff, 1878.

or molecular transformation also proves to be of a general and simple nature; the velocity being directly proportional to the surface of contact of the reacting parts of the heterogeneous systems and to the remoteness of the system from the point of equilibrium.* The velocity of chemical reaction and chemical equilibrium in heterogeneous systems represent no phenomena *sui generis*, the laws concerning them being only combinations of the above two laws.† The laws relating to equilibrium found their rational explanation and foundation in the thermodynamic researches of HORSTMANN, and more fully in those of W. GIBBS and VAN'T HOFF, whilst the laws applying to the velocity of reaction in homogeneous systems are the result of VAN'T HOFF'S thermodynamic considerations.

In all the above researches the phenomena of the velocity of chemical reaction and of chemical equilibrium are the outcome of those intrinsic properties of matter, always existent in and inseparable from it, which we usually call chemical affinity or chemical potential. It is known, however, that a system can be brought into a state of reaction, and that new systems and new equilibria can be formed, when energy from an external source, such as light or electricity, is introduced into it. The effect of an electric current upon a chemical system, *e.g.*, is determined by FARADAY'S law of electrolysis, whilst the thermodynamic connexion between chemical and electrical (and gravitation) energy has been developed by W. GIBBS.

The object of this investigation was to ascertain, if possible, the laws governing the velocity of chemical reaction and chemical equilibrium when this is caused by the introduction of light energy into the system. Is the velocity directly proportional to the amount of the light energy introduced or absorbed by the system in the unit of time, independent of the reacting masses or concentrations, *i.e.*, is the law here analogous to that of FARADAY for electrolysis, or is the velocity of reaction some function of the reacting masses? What are the laws governing chemical equilibrium as affected by light? It is evident that to furnish an answer to the above problems careful experiments bearing directly on the fundamental issues in question and a careful theoretical consideration of the results so obtained are absolutely needed. This is the more imperative as from the hundreds of reactions known to be caused or influenced by light‡ not half a dozen can be found suitable for quantitative measurements.

It soon appeared that the chemical reaction chosen for the study of the laws of chemical kinetics must be very simple and as far as possible uncomplicated by secondary phenomena. The chemical action observed must be caused by light alone, and stop when light is removed. BUNSEN and ROSCOE'S reaction ($H_2 + Cl_2 = 2HCl$) seems to fulfil these conditions, but inasmuch as no change of volume takes place, no

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* See M. WILDERMAN, 'Zeits. Physik. Chem.,' 1899, 30, p. 341, and especially 'Phil. Mag.,' 1901, July, p. 50.

† See 'Zeits.,' *loc. cit.*, pp. 363–382.

‡ See EDER'S 'Handbuch der Photographie.'

answer could be afforded to the question whether the velocity of reaction is a function of the varying masses or concentrations of the combining substances or not, unless the hydrochloric acid formed is as rapidly removed as it is formed during the reaction. A secondary reaction would thus take place which would complicate the principal reaction. For these and similar reasons* DAVY's reaction ($CO + Cl_2 = COCl_2$) was chosen for study. The reaction occurs only in light, the gases can be used in a dry state, and the volume of the mixed gases changes, two volumes of the original mixture producing one volume of the compound.

Since highly dried gases combine very slowly, it was obvious that an artificial source of light must be employed, which should be at the same time of great actinic power and susceptible of being maintained constant in its intensity for long periods. At the suggestion of Dr. LUDWIG MOND the acetylene light was finally decided on, as it is rich in actinic rays and its spectrum closely resembles that of sunlight. Apparatus was devised for producing a flame constant in intensity and composition. Arrangements were made for measuring the intensity of the light with an accuracy to 0·1 per cent., and suitable methods chosen for the preparation of pure chlorine and carbon monoxide. A preliminary study extending over two and a half years was made of the conditions under which the experiments must be conducted so as to give not only concordant but accurate results, *i.e.*, results free from constant errors. The general arrangement of an experiment was as follows:—

Pure, dry chlorine and carbon monoxide were freshly prepared in the dark, and there introduced into a reaction vessel, connected with a manometer to indicate the variation of pressure during the reaction. The reaction vessel was placed behind a quartz window, in a water bath kept at a constant temperature, and exposed to a powerful acetylene light. The acetylene light was kept of constant intensity and free from smoke by means of a special generator, balance governor, regulating tap, purifier and burner. The intensity of the acetylene light was measured by means of a Rubens' thermopile and the deflections of a galvanometer, and the observed values standardized by means of a Clark cell and manganin resistances. The variations of the pressure in the reaction vessel were read on the scale of the manometer by means of a cathetometer. After applying corrections for the variation of temperature of the bath, atmospheric pressure, &c., the experimental results representing the rate of formation of carbonyl chloride from chlorine and carbon monoxide were subjected to a theoretical investigation.

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* See MELLOR, 'Journal of the Chemical Society,' 1901, p. 227.

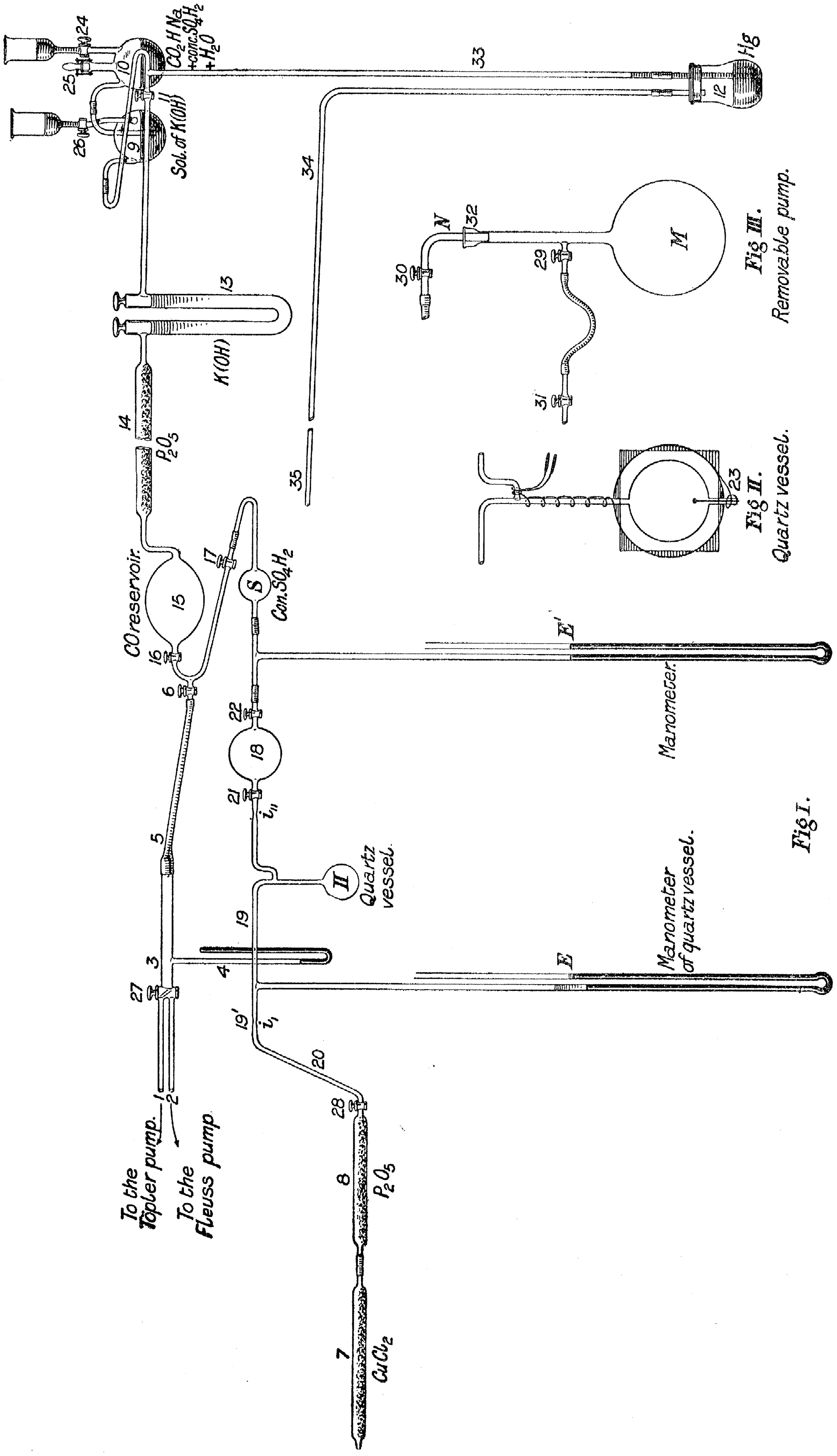

Fig III. Removable pump.

Fig II. Quartz vessel.

Fig I.

PART I.

General Arrangements for the Preparation of Pure Cl_2 and CO, and for Filling the Reaction Vessel. (See Diagram 1.)

A Töpler pump is connected with one arm (1) of the T-tube, and a double-cylinder Fleuss pump with the second (2), the third (3) carries the manometer (4), and is connected with the rest of the apparatus by tube (5). A 3-way tap connects either (1) or (2) with (6).

On the left of the diagram the apparatus for producing pure chlorine is shown. Tube (7) containing cupric chloride was heated by one small flame; the chlorine formed passes through tube (8) containing phosphorus pentoxide which is connected with the reaction vessel whenever it is to be filled with chlorine. Before filling the reaction vessel with chlorine, the cupric chloride and phosphorus pentoxide tubes were exhausted and heated till a vacuum of ·01 millim. was obtained. Chlorine was produced by heating the cupric chloride tube, the chlorine then removed, and a further supply prepared and directly used for the experiment.

On the right of the diagram the apparatus for producing pure carbon monoxide is shown. Vessel (10) contains sodium formate and concentrated sulphuric acid, vessel (9) contains a concentrated solution of potassium hydroxide. When the mercury tap (11) is closed, the carbon monoxide formed bubbles through the mercury in vessel (12). When the tap is opened it passes through the U-tube (13) containing pieces of caustic potash, then through the long tube (14) containing phosphorous pentoxide to the receiver (15), which was chosen of a large size so that the gas should be as little contaminated with air as possible. This vessel (15) was closed by the mercury taps (16), (17) and (6), and was further protected from contamination with air by the tube between the taps (16), (6) and (17) being filled with pure carbon monoxide. Special precautions were taken to keep the carbon monoxide in (15), (14) and (13) pure; while the carbon monoxide from the tube between (16), (6) and (17) was from time to time completely removed by pumping and heating, and the tube again filled with pure carbon monoxide from (15). Before filling the glass bulb (18) with carbon monoxide, every vessel containing the gas was first evacuated to about ·01 millim., fresh gas was again prepared and immediately used for the experiment.

In the middle of the diagram the reaction vessel (II) is shown, into which carbon monoxide and chlorine are brought together for exposure to light. This consists of a glass cylinder with ground flanges on which two parallel quartz plates are fixed, one in front and the other at the back. A capillary tube (19) connects the manometer E with the reaction vessel, and with the tube (20) through which the chlorine gas is passed from the cupric chloride tube into the quartz vessel. The latter is also connected with the bulb (18), (21) and (22) being mercury taps. The bulb (18) is connected with a manometer (E′) and is filled first with carbon monoxide. The pressure of carbon monoxide in (18) should be greater than the pressure of chlorine in the quartz vessel (11). By opening the tap (21) the carbon monoxide is allowed to pass into the quartz vessel (II). No chlorine, as direct careful tests showed, passes under such circumstances into the bulb (18).

I now pass to a more detailed description of the apparatus used.

The Reaction Vessel (fig. II.), was a glass cylinder of 3·65 centims. diameter, 3·6 centims. long (capacity = 41·26 cub. centims.), with flanges 6 millims. wide at each end (as in fig. II.). The flanges were very carefully ground so that the two perfectly smooth quartz plates, when placed on them, fitted perfectly, and an excellent vacuum could be obtained. The quartz plates, with parallel surfaces, 45 sq. millims., and about 2 millims. thick, were cut out perpendicularly to the optical axis, and were optically pure. The front plate turned the plane of polarisation to the left, the back to the right.

Since chlorine acts on any cement which could be used for the purpose of keeping a vacuum, the quartz plates were placed directly on the well-ground flanges of the glass cylinder, and melted Crookes' cement, consisting of beeswax and resin (proportions, 5 parts beeswax to 8 parts resin) put on outside where the outer edges of the quartz plates met the glass flanges, care being taken that the cement was properly melted and free from air. The corners of the quartz plates projecting over the flanges and those parts of the glass flanges which remain uncovered by the quartz plates were then covered up with melted Crookes' cement, the whole being heated and made smooth and firm by a very small flame. In this condition the vessel can preserve a very high vacuum for a very long time. The cement was then covered with a varnish of pitch in benzine to protect the cement from the action of water, and allowed to become thoroughly dry The outside of the cylinder was also covered with pitch so that light might only enter through the quartz plates.

In the capillary tube (23), at the bottom of the glass cylinder, an iron-nickel couple was fixed to measure the temperature of the gas in the inside of the cylinder during the reaction. Two very fine iron-and-nickel wires (about 0·1 millim. diameter) were made considerably thinner at their ends (0·05 to 0·02 millim.) by repeated alternate immersions in nitric acid and in water. About 1 centim. of the two very fine ends were twisted together and a trace of melted soft solder put on the extreme ends. On bringing it near a flame, the solder melted and ran down the twisted wires and was quickly shaken off, forming only a very thin film of solder between the wires. The soldered ends were then washed and all but 2 millims. of the connected ends were removed. The two wires were then covered with shellac and a thin layer of pitch. The very thin double wire (perhaps 0·2 millim.) was then passed through the very narrow capillary tube (23) projecting about $\frac{1}{2}$ millim. into the cylinder, and fixed at the bottom in the capillary tube by a trace first of pitch, then of Crookes' cement, and then again of pitch. This thermopile was very sensitive to variations of temperature, and does not interrupt any essential portion of the light on its passage through the quartz vessel to the back plate. The second iron-nickel thermocouple was wound outside the tube as near as possible to the first couple in the glass cylinder, the two iron-and-nickel wires being drawn up round the cylinder, and then wound up round the capillary tube. These wires were first covered with shellac and then with pitch varnish. The thermopile assumed the temperature of the air or gas, owing to its extreme thinness, with very great rapidity. Subsequently a thin, glass bulb of similar volume was used instead of the quartz vessel.

The capillary tubes used were of a very narrow diameter. The capillary tube E of the manometer was necessarily somewhat wider, so that the mercury might move easily, and rapidly assume equal levels in both arms of the U-tube. A length of 155·7 centims. of the capillary of one of the manometers contained 9·476 grams of mercury = 0·701 centim. The total volume of the capillary tubes in the manometer over the mercury during the experiments (20 to 50 centims., &c.) is very small in comparison with the volume of the cylinder of the quartz vessel, which is over 40 cub. centims., amounting to only a few tenths of 1 per cent. The manometer contained a layer of concentrated sulphuric acid (about 10 centims. long), enough to protect the mercury from the chlorine. The concentrated sulphuric acid freed the capillary tube from any specks of dust, thus enabling the mercury to move in it much more easily. The acid must be heated *in vacuo* after it is brought into the capillary to remove air and sulphurous acid. Only after the sulphuric acid has been heated *in vacuo* can a very high vacuum be obtained which will remain constant for any length of time. In filling the capillary tubes with the sulphuric acid and mercury, the part of the apparatus between (22) and (19′), which can be separated from the other parts, is kept almost in a horizontal position, the open tube of the manometer being connected with a tube dipping into a small beaker of mercury covered by concentrated sulphuric acid. Tap (22) being closed, tube (19′) is held over the mercury in the concentrated sulphuric acid till a few centims. of sulphuric acid rise in the tube, and then dipped into the mercury, allowing it to follow the sulphuric acid. If the mercury column is broken by sulphuric acid, the column is driven out from the capillary by forcing air into the vessel at (19′) until most of the acid is expelled from the capillary, when the tube is refilled. The capillary U-tube of the manometer was calibrated in the usual way. Since concentrated sulphuric acid adheres to the glass, the sulphuric acid column is shorter when the mercury is low and longer when it is high, especially if the mercury is moving rapidly up and down. During the experiment upon the velocity of reaction the movement of the mercury is so slow that uniform results are obtained; but a reading must be made of the levels of both mercury and sulphuric acid.

The density of the sulphuric acid used was easily found from the heights of the sulphuric acid and of the mercury in both arms of the manometer when exposed to the pressure of the atmosphere. The U-tube of the manometer was fixed on a glass scale silvered on the back to avoid parallax, the readings of the scale were easily made by means of a cathetometer to 0·05 millim.* As the experiments proceeded, it was found that there was no possibility of protecting, by means of mercury taps, the gas mixture in the quartz vessel from contamination with air for more than a few hours, even when to the mercury taps capillary tubes were added containing the same reacting gases as the quartz vessel, with a second mercury tap at each end. The tubes of the quartz vessel on both sides were sealed for this reason by means of a hand blow-pipe as soon as the quartz vessel was filled with the gas mixture. Later on the quartz vessel had to be abandoned altogether, chiefly for the reason that it could not be heated before filling the reaction vessel with the gases; more reliable results were then obtained with a thin bulb of very pure glass than with the quartz vessel.

Filling the Reaction Vessel with Carbon Monoxide and Chlorine.

Having read the position of the meniscus of the sulphuric acid and of the mercury on both arms of the manometer, the apparatus was exhausted, every part of it being heated to expel the air which persistently sticks to the glass walls of the apparatus. Since, however, the quartz vessel (owing to the Crookes' cement and pitch) could not be heated, the complete removal of the air was effected as follows:—Having connected the pumps through (1) and (2) with (6), the taps (6), (17), (22), (21) and (28) being open and the taps (16) and (11) closed, all the vessels (7), (8), (E), (II), (18), (E′), (S), (R), (19), (3), (2), (1) and (4) were exhausted first by the Fleuss and then Töpler pump, and all, except the quartz vessel (II), were heated. The concentrated sulphuric acid in (S) and over the mercury in (E) was also heated until no more gas was given off. In this way a high vacuum was obtained. The taps (6) and (28) were then closed and carbon monoxide passed from its reservoir (15) into the bulbs (S) and (18) and to the quartz vessel (II) until the pressure was about 10 centims. The carbon monoxide was then removed by exhaustion, (16) and (28) being closed until a good vacuum was indicated by the Töpler pump, when the vessels were again filled with carbon monoxide. This was repeated several times till the air was completely removed from the walls of the quartz vessel. Better results, however, were obtained when a thin bulb of pure glass was used and the bulb heated during the evacuation. But even in this case, after the first evacuation the bulb was filled with carbon monoxide

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* The mercury meniscus in the short arm always remains as clear as a mirror. From its position and an ordinary calibration of the capillary tube of the manometer, the variation in the mercury column can be determined with even greater accuracy than 0·05 millim. The readings of the mercury meniscus in the long arm of the manometer, together with the upper ends of the sulphuric acid columns in the two arms, enables the length of the sulphuric acid columns to be measured with an accuracy much exceeding 0·05 millim. mercury, considering that the specific gravity of the sulphuric acid is only about 1·85.

and evacuated to a high vacuum of about 0·01 millim. Taps (16), (17) and (21) were then closed, and chlorine prepared in (7) till the pressure in the reaction vessel became equal to about 10 centims. Tap (6) was connected with the removable pump (M), and (M) and (R) heated and evacuated, carbon monoxide sent into it from (15), again evacuated, and then (17) and (21) opened and the chlorine removed. The taps (17) and (16) were then turned off, (6) connected with the pumps, (R) evacuated, all vessels (13), (14), (15), (R), (S), (E′) and (18) evacuated, and carbon monoxide from (9) and (10) removed as far as possible, partly by opening tap (11) and then removing the same from (15), &c., partly by allowing the freshly-prepared carbon monoxide to bubble for some time in (12). The bulbs (15), (S) and (18) were then finally repeatedly filled, at one atmosphere pressure or more, with fresh carbon monoxide from (10) (prepared in the dark, only one incandescent lamp at a distance being used). The quantity and pressure of the carbon monoxide introduced into the glass bulb (18) is known from the volume of the bulb and from the indications of the manometer connected with it. The tap (17) was then turned off; the reaction vessel was next completely protected from light. The tap (28) was now turned on, and 1 or 2 centims. of the tube containing cupric chloride was then slowly and cautiously heated (in the dark), so as to evolve chlorine and to allow it to pass to the reaction vessel at a slow rate. From the indications of the manometer the amount of chlorine introduced into the quartz vessel was known, and the production of chlorine was stopped by removing the burner from the tube as soon as the desired quantity of chlorine, which is very small, had been introduced into the quartz vessel. The capillary tube was immediately sealed up with a hand blow-pipe at $i_{/}$—where it had been previously drawn out. After the heated parts had cooled down, the position of the meniscus of the mercury and of the concentrated sulphuric acid was read in both arms of the manometer by means of a faint light, as well as the temperature of the room and the barometric pressure. The manometer (E′) was again read, the tap (22) closed, the tap (21) opened, and the carbon monoxide, which is at a greater pressure in (18) than the chlorine in the reaction vessel, was slowly allowed to pass through the drawn-out capillary tube (at $i_{//}$) to the quartz vessel, so as to keep the SO_4H_2 column over the mercury the whole time long enough, and when the mercury no longer moved in the manometer (E), the tap (21) was closed and the capillary tube sealed at $i_{//}$—where it was previously drawn out. The vessel was again allowed to cool and the temperature and pressure readings again noted.

From the variation in the height of the manometer the quantity of carbon monoxide introduced into the quartz vessel was known. The volume of the bulb (18) is immaterial, if it is of sufficiently large size to allow of the introduction of any desired quantity of carbon monoxide into the reaction vessel. The bulb (18) was then taken off, the end with the tap (21) immersed in a beaker containing a solution of potassium iodide, and the tap opened. It was found that with the above arrangements, *i.e.*, with a thin capillary tube drawn out at ($i_{//}$) and with an over-pressure of carbon monoxide in (18), not a trace of iodine (*i.e.*, of chlorine) can be detected in the bulb (18), even with such a sensitive reagent as freshly-prepared starch solution. By leaving the tap (21) intentionally open for half an hour, only small traces of chlorine could be detected in the bulb (18). This shows that the diffusion of the heavy chlorine gas to the top through a very thin capillary into the vessel containing carbon monoxide, which is a vacuum for chlorine,* is extraordinarily slow. For this reason the method of filling the vessels must not be reversed, *i.e.*, we must not fill the quartz vessels first with carbon monoxide and then with chlorine from the bulb, nor can we uniformly mix the two gases in the two vessels by opening the tap (21), even when the capillary tube is large, a method adopted in many similar investigations, but which was found, at any rate in this case, to be wrong.

The Removal of Chlorine from Tubes (7) *and* (8) *and from the Quartz Vessel. Removable Pump.* (See fig. 3, Table I.)

Before passing to the description of the methods of preparation of pure chlorine and carbon monoxide, a few words must be added as to the mode in which chlorine can be completely removed from the vessels before a new experiment is proceeded with. The removal of carbon monoxide is a simple matter—this being done by the Töpler pump, but chlorine cannot be removed by the Töpler pump, because even small quantities of chlorine instantly attack the mercury. All attempts to protect the mercury pump by inserting tubes with precipitated copper or mercury for the absorption of the passing chlorine completely failed. This, however, was effected in the following manner:—The vessel (M) was connected through (30) with the vessels containing chlorine and was heated and evacuated through the taps (29) and (31), connected with (15) by means of a Töpler and Fleuss pump, and while the tap (30) was turned off, the taps (29) and (31) were then turned off and the tap (30) turned on. A great part of the chlorine passes from the vessels containing it into the

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* In this research the velocity of combination of chlorine and carbon monoxide, as a function of the reacting masses, had to be studied. A horizontal gauge, as used by Bunsen and Roscoe, could not be employed, because very great variations in the reacting concentrations or masses of the gases, amounting to 70–80 per cent., had to be studied. Thus a mercury manometer had to be employed. To be able to carry out this research, in view of the chlorine attacking the mercury, advantage was taken of the extremely slow diffusion of chlorine, which in concentrated SO_4H_2 is still smaller than into a vessel of carbon monoxide, which is a vacuum for chlorine. If the column of the concentrated SO_4H_2 over the mercury in the manometer is taken long enough (10 centims.), and care is taken that the filling of the quartz vessel with chlorine or carbon monoxide is very slow, so that the concentrated SO_4H_2 should not remain on the walls of the capillary tubes, but have time enough to run down, then we find that the dry chlorine will not attack the mercury for days, and even weeks. Sometimes we find after a longer time that the mercury meniscus becomes a little dull, without, however, losing its shape, and without the mercury losing its mobility, and without interfering with accurate reading.

vessel (M). The tap (30) was again shut and the india-rubber tube removed from the tap (31). After opening tap (29) and carefully allowing air to pass into (M), the vessel (M) was detached from the rest of the apparatus at (32), where the ground tube (N) perfectly fitted into the neck of (M). The chlorine was then removed from (M) by blowing through a tube introduced into it through its neck; (M) was now replaced on the tube (N) and evacuated. Chlorine was aspirated into (M) and blown out until a pretty high vacuum was obtained in all the apparatus. Air was then allowed to pass into the vessels which contained the chlorine and the whole again evacuated directly by the Fleuss pump, and finally to a high vacuum by the Töpler pump, in the ordinary way. Chlorine can now be again prepared from the copper chloride in (7).

Experience has shown that the only and perfectly reliable way of getting pure gases free from any contamination with air is to remove, before each experiment, the chlorine and carbon monoxide (though they are apparently perfectly pure) from all the heated vessels as completely as possible, and to immediately prepare perfectly fresh chlorine and carbon monoxide. As soon as they are prepared they are sealed up in the quartz vessel (or the glass bulb used instead of it) as quickly as possible.

The Preparation of Pure Gases.

A. *Preparation of Pure Chlorine.* (See (7) and (8) in fig. 1, Table I.)

In order to get chlorine free from any admixture of air and water vapour, which prove to be most fatal to the gas mixture, and also of any other gas, the ordinary simple methods could not be employed. It was therefore prepared either from platinous chloride or cupric chloride in a vacuum. Cupric chloride, suggested by Dr. Ludwig Mond, has great advantages in comparison with platinous chloride; it is very much cheaper, water can be easily removed from it, and there is no danger that oxygen or hydrogen from the air will be absorbed by the residue, as is the case with platinum. Besides this, occluded gases cannot be completely removed from the platinum unless by exhaustion at a temperature higher than that at which platinous chloride gives off chlorine. Cupric chloride, so called "purissima," always contains hydrochloric acid. This, it was found, cannot be completely removed. The cupric chloride was, therefore, prepared from precipitated copper and chlorine, taking all precautions to avoid conditions which might contaminate the product with hydrochloric acid. Finely divided copper, precipitated from a solution of copper sulphate by means of zinc, was placed in a long combustion tube drawn out at both ends. The hydrogen current, first washed and dried, was passed over the copper (heated to a dull red heat) for several hours to remove the film of oxide. The tube was next sealed at one end and exhausted, and air was then allowed to pass into the tube, which was again exhausted and heated. The hydrogen was thus completely removed.

The end of the tube was then opened and a current of chlorine, prepared from manganese dioxide (freed from carbonates) and concentrated hydrochloric acid, passed through two wash-bottles of water and two bottles of concentrated sulphuric acid, was passed over the reduced copper.

Chlorine combines with copper in the cold, but as the reaction progresses the copper and tube become heated from one end to the other. The heat developed is usually so great that the cuprous chloride formed melts to a cake. When the contents of the tube have become green, the tube is broken, the mixture of cuprous and cupric chlorides is powdered and placed in a Jena tube drawn out at both ends. The tube is now heated for its whole length to about 250–300°, and chlorine is allowed to pass over it for a long time, the tube being shaken from time to time, when more chlorine is absorbed. The whole mass is then allowed to cool in the current of dry chlorine. From the increase in the weight of the tube and the weight of the copper taken, the amount of the cupric chloride formed can be calculated, and, if necessary, the operation of passing chlorine over the heated mixture of cupric and cuprous chlorides is repeated. There is no necessity for the whole mass to be transformed into cupric chloride. A current of air is then drawn through the tube to remove the chlorine, for the reason stated above, and then one end of the tube is sealed up.

Tube (7) with cupric chloride and cuprous chloride thus prepared is now ready to be used for the experiment; it is placed on a combustion furnace, one end of it being connected by means of a piece of india-rubber tube used for vacua to tube (8), containing phosphorus pentoxide, and the india-rubber covered with Crookes' cement.*

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* It was found that no tube of soft glass could be used, the atmospheric pressure outside pressing the glass in at the places where the tube was heated. Thus a tube of hard glass had to be used. This, as known, cannot be joined with the soft glass of which the glass cylinder of the quartz vessel and the capillary tubes are of necessity made. Since it was found that air (oxygen) and water vapour are just the gases which are most fatal for the gas mixture, the heating of cupric chloride in a vacuum was inevitable, and no other method could be employed instead. Luckily, the amount of chlorine gas required for each experiment was exceedingly small, and only about $\frac{1}{200}$ gram. mol. of cupric chloride had to be decomposed for each experiment, *i.e.*, only 1 or 2 centims. of the tube (7) had to be heated, and, since the filling of the quartz vessel with chlorine and carbon monoxide had to be carried out (for reasons given above) slowly, and cupric chloride decomposes at a comparatively low temperature, this centimetre or two of the tube had to be heated slowly and cautiously with only a comparatively small flame. Tube (7) was heated at the sealed end, which is more removed from tube (8), and the glass of (7) is made to meet the glass of (8). Under these conditions not only is the glass of (7) and (8), where they meet, quite cool, but the tube (7) is so already, being 30 or 40 centims. removed from (8). The gas passed the drawn-out cold tubes (7) and (8), where they meet, with the india-rubber collar on the top, for only about 10 minutes. Under these conditions no traces of the action of chlorine upon the india-rubber collar can be found on cutting the same, or by chemical analysis. Chemical analysis, however, can give us little information about small impurities when the quantities of gas are so small as those which I had at my disposal. There, however, still remains a superior analysis for impurities, when no chemical or physical method can be of any more use, viz., the possibility of getting regular curves and a velocity constant. This analysis showed that either the chlorine is absolutely free from any impurities, or that they are so small and of such a kind as not to interfere with the phenomena under consideration.

Before the chlorine was prepared for the experiment the tube containing cupric chloride, (7), and the tube (8), with phosphorus pentoxide, were connected with the tube (20) leading to the quartz vessel (II), and heated and exhausted till the pressure was reduced to not more than 0·01 millim. In this way the air was first expelled from all vessels and from the cupric chloride. The tap connecting all these parts with the mercury pump was then shut, and 1 or 2 centims. of the tube (7) gradually heated nearly to red heat and chlorine slowly evolved. When the manometer indicated that the pressure of the chlorine was about 10 centims., the heating of (7), and with it the formation of chlorine, was stopped. After removing the chlorine by means of the removable pump, fresh chlorine gas was admitted. This process was repeated to expel the last trace of air, when chlorine was again introduced and sealed up in the tube.

B. *Preparation of Pure Carbon Monoxide.* (See (9), (10), (13), (14) and (15) of figure (1), Table I.)

Carbon monoxide gas was prepared from sodium formate (35 gr.), and a mixture of concentrated sulphuric acid (200 gr.) and water (100 gr.), the proportions given by Lord RAYLEIGH. Carbon monoxide is produced when the mixture is heated, and its formation is stopped when the mixture is cooled down to the ordinary temperature, so that the same solution can be repeatedly used for the production of carbon monoxide.

The experiment was so arranged that neither the vessels nor the liquids used for the reaction contained any air. The sodium formate was introduced into (10) through the neck (25), the stopper of which was so well ground that when covered with vaseline it could stand a vacuum for any length of time when the pressure of the carbon monoxide in the vessel was one atmosphere. Vessels (9) and (10) had the U-tube (13) containing pieces of caustic potash, the long and wide tube (14) containing phosphorus pentoxide and the carbon monoxide reservoir (15), as well as the tube (R) between (16), (6) and (17), the purpose of which was to protect the carbon monoxide in (15) from contamination with air, were all heated and completely exhausted. During this taps (11) and (16) were open, and taps (24), (26) and (17) were turned off.

The air had next to be removed from the channels of the taps (24) and (26). This was affected in the way shown in figure (4). After all the vessels (9), (10), (13), (14), (15), &c., were evacuated to a high degree, a capillary tube (t') with the tap (T) at one end and a piece of india-rubber tubing (R) at the other drawn-out end, was pressed tightly into the tube of the funnel of (10), and another similar one into the funnel of (9). (T) was turned off, (24) opened. After this the same was done with tap (26). Since the volume of the channels in the taps (24) and (26) and the space above them is perhaps only 0·3 cub. centim., while the volume of all the vessels is about 1500 cub. centims., the pressure in all the vessels is only about 0·15 millim. The taps (24) and (26) were then closed and tap (T) opened to allow the removal of the tube (t'). A little water was brought over the taps at (24) and (26). Vessels (9), (10), (13), (14) and (15) were then again brought to a high vacuum, and it is evident that the air still contained in the channels of the taps (24) and (26) (the pressure in them being 0·15 millim., and the volume about 0·02 centim.) could later on introduce, when opened to allow liquid to pass through them to (9) or (10), a contamination with air into the vessels of only about $\frac{0\cdot15 \times 0\cdot02}{1500} = 0\cdot0000002$ millim. Taps (16), (6), (17) and (11) were now closed and a concentrated solution of caustic potash in water, first boiled in a vacuum and freed from air, and kept in an evacuated flask, poured into the funnel of (24). Some of the caustic potash solution was forced into (9) through tap (24), but not so as to reach the tube leading from (9) to (10), to prevent the vapour pressure in (9) from pressing the solution into (10). Into the funnel of (24) a mixture of two parts of concentrated sulphuric acid and of one part of water boiled out *in vacuo* was quickly introduced. About 250 cub. centims. of the sulphuric acid solution was rapidly passed into (10), and a burner placed under it; more caustic potash solution was again passed into (9) until tube (32) in (9) was covered about 2 centims., when the vessel (10) was rapidly heated by passing a flame round it. In this way the caustic potash solution may be prevented from passing into (10) through tube connecting (9) and (10), and if a trace of it does pass into (10) it is subsequently neutralised by the sulphuric acid and does not affect the result in any way. Vessel (10) must be heated on all sides to avoid bumping. Tap (11) is turned off during the formation of carbon monoxide to prevent the distillation of water into vessels (13) and (14) containing solid caustic potash and phosphorus pentoxide. The carbon monoxide formed in (10) passes through a solution of caustic potash in (9), leaving there any traces of carbonic acid or of sulphurous acid, and it presses the mercury in (33) down until it begins to bubble through the mercury seal in (12), passing from there through tube (34) to the open air. The carbon monoxide is then pumped up at the end (35) till the pressure in (8) and (10) becomes about 150 millims., the carbon monoxide which is still being formed bringing the mercury in tube (33) down again till it begins to bubble through the seal in (12). Repeating this several times, we expel the last traces of air from the vessels and liquids. The vessels (13), (14), (15), (5) and (18) were then filled with carbon monoxide. Tap (11) is partially opened, so that the carbon monoxide should not bubble too rapidly through the solution of caustic potash and only slowly

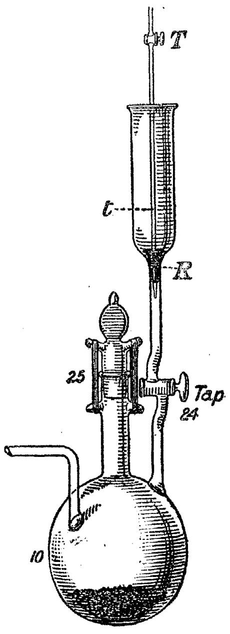

Fig. 4.

through the concentrated sulphuric acid in the tilted vessel (S). After a short time, when the mercury had risen in tube (33) about 10 centims., tap (11) was turned off again. This is done because the formation of carbon monoxide goes on more quickly and regularly as the pressure of carbon monoxide increases. When the newly formed carbon monoxide again begins to bubble through the mercury, the tap (11) is again opened and shut as before; this is repeated until the pressure of carbon monoxide becomes everywhere a little over one atmosphere, *i.e.*, the mercury column in (33) does not rise again when the tap (11) is opened, and carbon monoxide continues to bubble through the mercury (if a still higher pressure is desired the tube at (35) is closed). The taps (11) and (16) are now closed (open at 35), allowing the carbon monoxide gas to bubble through the mercury and escape to the air. After removing the burner from (10) it is rapidly and uniformly cooled on all sides by means of a wet cloth, until the formation and bubbling of carbon monoxide through the caustic potash ceases. The tube (4) is also filled with carbon monoxide at the same time in order to protect, subsequently, the carbon monoxide in (15) from contamination with air. The glass tubes of the different parts of the apparatus are directly joined together without the use of india-rubber tubes, and all the taps have mercury seals.

In the funnels of (9) and (10) sufficient caustic potash solution and of sulphuric acid solution is always left, and taps (24), (26), and (25) should be so exceptionally well ground that even after many weeks (when covered with vaseline) the taps remain quite transparent. The object of these precautions was that pure and fresh gas might be prepared quickly for each experiment. Carbon monoxide gas, which had been kept in the vessels for even small lengths of time, was never used. When an experiment was made, vessels R, S, (18), E, (15), (14), (13), &c., containing pure carbon monoxide, were always first evacuated, heated, and the freshly-prepared carbon monoxide passed directly into the bulb (18), allowing it to bubble slowly through the concentrated sulphuric acid in (S) as described. The tap (22) was then turned off, (21) turned on, and then the capillary tube (19) at $i_{\prime\prime}$ was immediately sealed up with a hand blow-pipe.

PART II.

ARRANGEMENTS FOR AN ACETYLENE LIGHT OF ABOUT 250 CANDLE-POWER OF CONSTANT INTENSITY.

Generator. (Arrangement for Constant Pressure.)

Acetylene generators, although they have some advantages over the ordinary gasholder, have also some disadvantages; firstly, because every time a fresh container of carbide is used, a fresh portion of air from the container is mixed with the gas, and though the volume of the container is very small in comparison with the volume of the acetylene gas in the gas-holder, still the mixture is undoubtedly a source of error, and special precautions have to be taken to remove the first portion of the acetylene formed from the container, so as to keep the composition of the gas during the experiments as constant as possible. Secondly, the pressure of the gas from such a generator varies very considerably in comparison with that supplied from large gas-holders. The generator used was the so-called "Incanto," by Messrs. THORN and HODDLE, with variations of 10 per cent. in the pressure of the gas delivered. This variation in pressure was found to be due to the strain of the floating balls on the

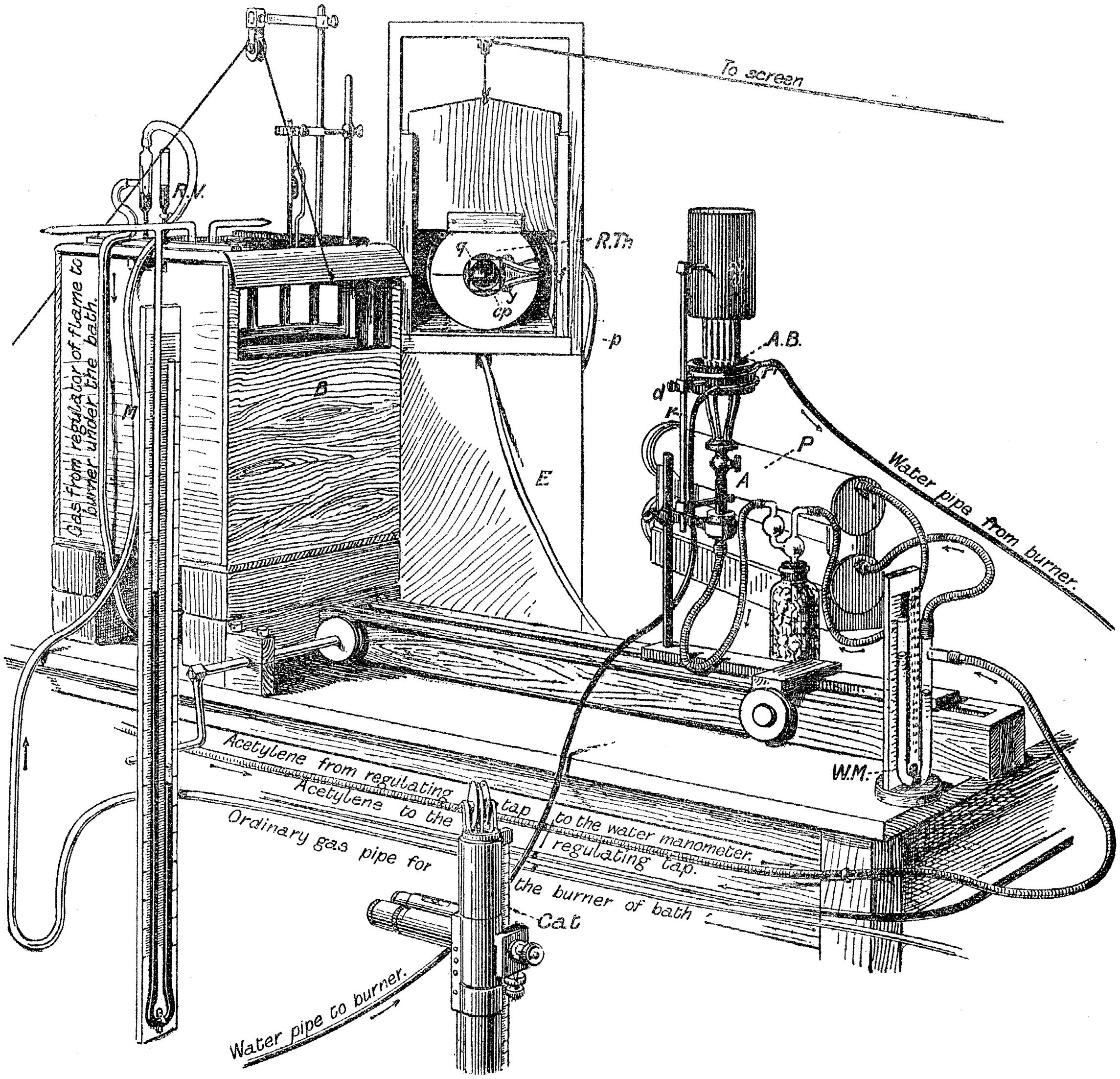

Fig. 5.

Sketch of Acetylene Burner and Purifier, Thermopile, Reaction Vessel, Bath, Water Manometer, and Cathetometer.—A.B., acetylene burner; P, purifier; R.Th., Rubens thermopile; B, bath; R.V., reaction vessel; M, mercury manometer of reaction vessel; Cat., cathetometer; W.M., water manometer.

chain of the generator, but a modification reduced the variations to about $1\frac{1}{2}$ per cent. The axis x (fig. 6) on which the ball L turns, was filed up till the movement of the ball in the axis was easy, and β, which guides the balls, as well as the stem of L at α, were then filed and clamped to give the ball a perfectly free movement up and down, but not much side play. Sheets of lead (s) were then fixed round the stem as near to the balls as possible, and the weight carefully adjusted so that a small additional weight of about 10–15 grammes placed near the balls should draw them quite down and open the valve, and that the removal of this weight should bring the balls up again, closing the valve. The modified generator gives, without a balance governor, for the heights of the bell out of the tank, between 16·5 centims. and 5 centims. (these are the limits within which the bell of the gas-holder chiefly varies in its height during the production and consumption of gas), a variation of only 1·5 millim. for 100 millims., *i.e.*, of $1\frac{1}{2}$ per cent. These variations of the pressure were further reduced by the balance governor.

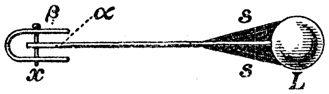

Fig. 6.

It was found that with a burner of such a candle power as I had to use (about 12 × 20 = 240 candles), a pressure of about 4 inches is necessary (instead of the usual 2). For this the upper chamber of the gas-holder had to be almost filled with water, leaving only space sufficient for the expansion of the water (in the winter care must be taken that the water does not freeze when the gas-holder is in the open air; more free space or a salt solution must be used). The gas generator was placed on the roof of the laboratory; from the generator a lead pipe brought the gas to the room; first to the balance governor, from the balance governor to the regulating tap, from the regulating tap to the water manometer WM, and then to the purifier; here it passed over the purifying substance of the lower cylinder, then of the higher cylinder, and thence to the burner.

The Regulating Tap to counteract the different sources of error was of the ordinary type. One tap, α, must always be quite open, when acetylene is consumed during the experiments. By turning another tap, the quantity of gas passing per unit of time to the burner is regulated, and the adjustment is indicated by the pointer on a fixed scale of 90 degrees. The purpose of this tap was to adjust the supply of gas to the burner so that the intensity of the acetylene light should, under varying conditions, always be kept the same. A series of conditions affect the intensity of the acetylene flame and necessitate the use of a regulating tap, such as the variation in the diameter of the outflow tubes in the nipples of the burner or the variation of the atmospheric pressure, which though in one and the same day hardly ever varying more than 1 or 2 millims., changes during a longer period considerably. There is another source of error of an irregular but temporary nature which also necessitates its use: the admixture of air when a new container is used. Everything was done to remove this source of error at its source. When a new container was introduced, the tap supplying water to the same was opened, and the cross-bar of the container pressing a metal plate on the india-rubber ring somewhat loosened. Water entered the container, the tap was turned off, and the acetylene with the admixed air allowed to escape between the metal plate and the india-rubber ring. This was repeated two or three times. In this way the air was expelled from the carbide containers so that when the cross-bar was tightened up and the tap opened again, no appreciable effect of the new container upon the acetylene ought to have taken place. With such precautions this source of error quickly disappears, owing to the gas-holder, leading pipes, balance governor, purifier, and burner containing a great quantity of pure acetylene—as can be seen from the observed intensity of light read from the deflection of the galvanometer. Variations, however, still existed, and sometimes required to be adjusted by the regulating tap. Another possible source of error was the variation in the composition of the gas, arising from the carbide used not being always of the same quality (it is not certain that such a source of error does exist). This was counteracted by the adjustment of the regulating tap.

These adjustments were always guided by the indications of the deflection of the galvanometer.

Water Manometer. (See fig. 5.)

Since it was necessary to work with a pressure of about 4 inches when the tap of the burner was shut, and of about $2\frac{1}{2}$ inches when it was open, 0·1 millim. variation in the height of the upper and lower side of the water manometer would indicate 0·2 millim. in 25 millim., *i.e.*, 0·8 per cent. variation in the pressure of the gas. Its chief purpose is to indicate in a quick manner, whether all the apparatus connected with the supply of the acetylene gas to the burner is in good working order.

The Acetylene Burner. (See fig. 5.)

All attempts to get a light of a great candle power, which would remain of a constant intensity and composition have been, as far as I know, unsuccessful up to the present. We have now standard lights of 1 or 10 candle power, but we have none of 200 or 1000 candle power, since the light of the arc varies considerably both in intensity and composition. The object here was to obtain a light of, say, 200 or 500 candle power, or of any other intensity desired, which would remain constant in its intensity and composition for any length of time, which could at any time be easily adjusted with great accuracy to the desired intensity, and which could be used with ease in the ordinary work of a laboratory. With the burners on the market which were tried, the gas is always passed either through a very thin slit giving a flat flame, or through two thin pinholes—the two gas streams meeting in one point, and giving again a thin flat flame (24–30 candle power). This is done in order to get the surface of the flame in contact with the air as large as possible, to obtain complete combustion and as white a flame as possible. It was found that after

24 hours' use—often even after much less—the candle power of the burner, either with the slits or pinholes, was no longer the same, and very often the slit or pinhole was already so much carbonised that the flame began to smoke; on the contrary, pinholes with a larger diameter, giving 40–50 candle power the pair, require a very much longer time before they become carbonised and begin to smoke, though even their candle power also diminishes with time. Since the form and even the thickness of the flat flame changes continuously, we can only get a constant light by cutting out a piece from the middle of the flame for a certain time, screening all the rest of it. Since we cannot get one flat white flame, by means of several gas streams directed to the same point, of more than 60 or 70 candle power, the increase of thickness or of the size of the flame beyond the 70 candle power being always accompanied by the formation of smoke, we could thus, in the best circumstances, not get a constant flame of more than 20 candle power, a candle power not very different from standards already existing. On the other hand, it was impossible with several flat flames to get one light of great intensity in a small space, since the flames cannot be placed very near to one another (owing to the form of the burner), and a flame of 200 or 250 candle power (12–15 nipples) necessarily occupies a very large area. If we further consider that each of the flames is different from the others in size and form, and that the flame of any one burner soon changes in form and size, and that only a small part of each could be cut off securely by a screen so as to give a constant light for some time, it is evident that the number of lights or nipples which would be required for a 200–250 candle power light to remain constant would be about 40 or 50. Assuming that even the greatest care be taken in placing the burners and screens on as small an area as possible, still the burner would occupy too much space, and no point or line could be calculated from the different lights which could theoretically be assumed to be the point or line from which the total light was coming.

The burner which was ultimately constructed free from these difficulties is that shown in the drawing (fig. 5).

The wide tube A of the burner is divided into four narrower tubes as shown, leading at intervals of 90° into the channel of a hollow ring cut in the brass ring. In the hollow brass ring (AB) 12 small brass pieces containing capillary tubes were fixed, and in the end of the brass pieces nipples were fixed. Each nipple has one round pinhole of about 15 or 20 candle power; the holes are parallel to each other, and each gives a flame in the form of a straight thick line of a few millimetres diameter and of a few centimetres in height. Round the brass ring a brass jacket is fixed, forming a hollow ring connected with the tubes r and r'. Water runs continuously through the hollow ring of the burner, which thus remains cool, in spite of the fact that flames of about 200–250 candle power are concentrated in a very small area. Using this arrangement of the burner, we find that the acetylene flame becomes perfectly pure and clear, and remains so for any length of time, even when the nipples have pinholes of only 15 or 20 candle power each. The clear circular flame so obtained consists of lines interrupted by narrow air spaces. Having all twelve lines in a narrow circle of only 1 or $1\frac{1}{4}$ inch diameter, at equal distances from one another, the direction of all the flames perpendicular, and the flames of equal length, though, perhaps, of not quite the same thickness, we can safely assume that the light comes from a perpendicular line drawn through a point near the centre of the narrow circle.

Since the error arising from small variations in the thickness of the lines cannot possibly in this case be greater than 1–2 millims. in the distance, this can, for the distance we have to use ($\frac{1}{2}$ to 2 metres), be completely neglected. The variations in intensity in the line of the flame proved to be due chiefly to variations in its top; by means of the chimney γ, all the top parts of the line-flames are cut off. Owing to the draught the lines are straightened and the air supply increased, while the products of combustion are removed and a clear white flame, remarkable for its constancy and brilliancy, is obtained. The screen and chimney γ can be moved higher or lower by means of the screw d, so as to get not only a constant flame with the photometer, but a flame of the desired intensity, the rest of the adjustment of the intensity being produced by means of the regulating tap. Besides the upper part of the flame, the lower part was also cut out by means of an adjustable short cylinder, which was also water-jacketed and connected with the water jacket of the burner.

Thus, with the simple arrangements described (generator, balance governor and burner), a source of light of 200–250 candle power (or 500 candle power and more, according to the number of nipples employed) can be obtained, which will remain constant, within 1 or 2 per cent., for a considerable time without regulation or adjustment.* By means of the regulating tap and measuring instruments, the intensity of the light can be adjusted with an accuracy to 0·1 per cent., and even much less.

THE GENERAL ARRANGEMENTS USED FOR THE MEASUREMENT AND ADJUSTMENT OF THE INTENSITY OF THE ACETYLENE LIGHT.

The Principle of the Method. Acetylene as a Universal Standard from 0·1 or 1 to 500 or 1000 Candle Power.

The light of the acetylene burner, which is placed at a certain distance from the thermopile, is allowed to fall on the exposed junctions of the Rubens thermopile (with 40 iron-constantan junctions), which is connected with galvanometer. A second measurement is made directly after by means of a Clark cell and standard

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* It should be noted that with the increase of the candle power of the burner, a greater pressure of the gas (in the gas-holder, &c.) is necessary for getting the best conditions for the flame.

manganin resistances (manganin 100,000 ohms, 6 ohms in the shunt were used, as shown in the diagram; the coil of the galvanometer, also of manganin, is 3 ohms). These resistances give, under the conditions of experiment, a sufficient deflection (about + 15 centims. to − 15 centims.), so that the value of the deflection caused by the acetylene light is always measured in standard units, independent of the sensitiveness of the galvanometer, &c. (the diagram also shows that the difference between the temperature in the quartz vessel immersed in the bath, owing to the reaction which takes place in it, and that in the bath is also measured with the same galvanometer by means of iron-nickel thermocouples; this, however, has nothing to do with the photometer itself).

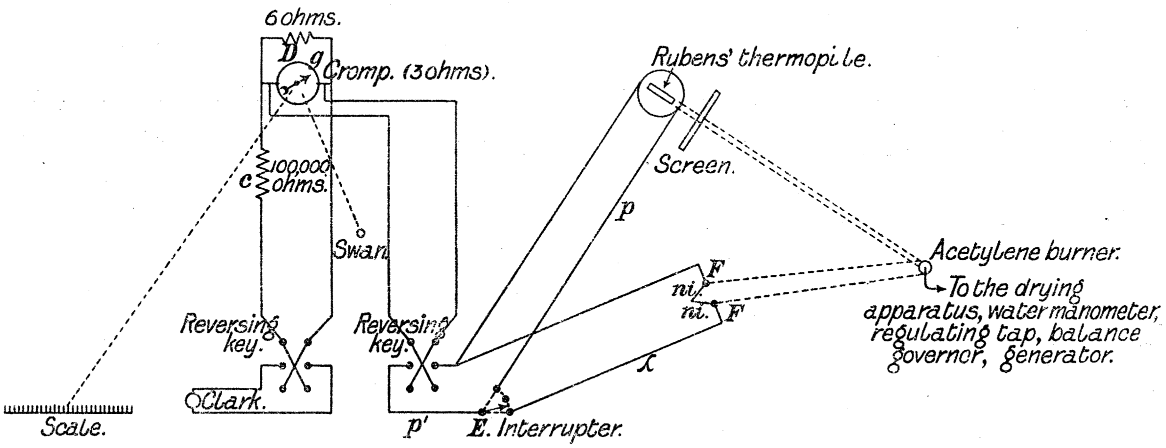

Fig. 7. Diagram to show arrangement of apparatus.

The principle of the measurement of the light intensity consists in its determination objectively by means of the deflection of the galvanometer and standard units (Clark, manganin resistances). We believe that if two sources of light (say acetylene gas) at a fixed distance, say 1 metre from the plane containing a given thermopile (with a given number of iron-constantan junctions), in the same relative position to the thermopile (the lines of the flames being parallel to the line of the exposed junctions and seen in the same position from the narrow tube in the double copper cylinder of the thermopile), give, or are made to give, the same deflection in standard units, then the intensity of the lights must be the same, provided they are quite pure and free from smoke and that the burner is cool. We assume that the heat effects of any source of light upon the exposed junctions of the thermopile, *i.e.*, the rise of their temperature, will be directly proportional to the amount of light falling upon them, *i.e.*, to the intensity of the light. This point is of primary importance. A careful theoretical investigation of it was absolutely necessary, and the investigation confirmed the conceptions. The electromotive force of the thermopile being thus directly proportional to the difference of temperature of the thermo-junctions exposed to the light, and of those which are left in the dark, the intensity of the light of a given source of light must be directly proportional to the corrected deflection of the galvanometer (or to the tangent of the angle), and can be measured by it.

It should be remarked that this objective method of measuring the intensity of light by means of a thermopile (or bolometer), and of checking it by means of a Clark cell and known standard resistances, measures the total heat energy produced by the given source of light in the thermopile, and thus differs from the other methods of measuring the intensity of light, the ordinary photometers, based upon the physiological effect of the light upon the eye. No doubt there is a distinct difference between the two; an acetylene light which we physiologically perceive, say of 16 candle power, is very much cooler than a 16 candle-power coal-gas light. The temperature to which the exposed junctions of the thermopile will be raised by the rays of flames of the same candle power, but from different sources of light, will therefore be different, the more so as the colour and composition of different lights are also different. Properly speaking two lights from two different sources (say acetylene and coal gas, or arc light) can neither be compared physiologically on account of their different compositions, nor in the objective way by means of a thermopile or bolometer, as given above, and no light can be compared except with a light of the same nature. For comparison of two lights of the same kind there can be no doubt that the objective method by means of a thermopile or bolometer is by far more accurate and reliable than measurement in the physiological way. As, however, for many practical purposes, the intensity of different lights has almost always to be expressed in candle units, different sources have to be compared and measured in this physiological way as far as it is practicable. In this photometric work, at any rate, all the standard units for comparison, the small as well as the large ones, ought to be correct multiples of one another, *i.e.*, ought to be all from the same source of light and of the same composition. Acetylene, as far as we know, is the only source of light which gives reliable standards from very small units, such as 0·1 or 1 candle power (when only a part of the line is used) up to very great units, such as 500–1000 candle power (when many lines on a space of about 2 inches in diameter should be used), and, except the burners, the same arrangements can be easily manipulated for fixing and adjusting all the standards in an absolutely correct and objective manner, as described here.

The author now passes to the description of the thermopile and of the other parts of the arrangements, indicated by the above diagram, which were used for measuring the intensity of the acetylene light.

The Thermopile (*or Bolometer*). See fig. 5.

A detailed description of the thermopile used is given by RUBENS in the 'Zeitschrift für Instrumentenkunde,' 1898, pp. 65–69, but a few data with regard to it must be given here.

The thermopile has 40 thermo-junctions* of iron and constantan, on an area of 2 centims., 20 of them in one line being exposed to the light, and 20 (10 in one line on each side of the line of the junction exposed to the light) remaining in the dark. The wires used are very thin (0·1 to 0·15 millim.), and the places of the junctions (those exposed to the light as well as those remaining in the dark, are hammered to little thin round plates (0·5 to 0·8 millim. diameter) so as to increase their sensitiveness to variation of temperature, and are made dead black. Before the line of junctions exposed to the light there is a small and then a larger cone of polished nickel, placed opposite and near the line of junctions, which causes a greater quantity of light to fall upon the junctions. The electromotive force of the thermopile is 0·00106 volt per 1° C.

In connection with the Rubens' thermopile a Crompton's dead-beat galvanometer was used, in order to avoid the numerous disturbances experienced by galvanometers other than that of the D'Arsonval type, and its sensitiveness was adjusted to get a sufficiently great deflection of the spot of light—not to get the greatest possible deflection, but to arrange the measurements of intensity so that after they were brought to a great accuracy, say of 0·1 per cent., the measurement should be made in an easy, steady, and reliable manner, and independent of numerous obstructive influences lying beyond the thermopile itself. This meant that special precautions had to be taken with both the thermopile and the galvanometer.

Whatever form is given to the thermopile, the next precaution, especially when a sensitive thermopile (or bolometer) is used, is to protect it from the influence of the surrounding medium, so as to secure concordant results. The junctions which are exposed to light are necessarily much more exposed to all sorts of air currents than those protected and covered from the light, and are also more subjected to the influence of the variation of the temperature of the room. The unavoidable continuous use of the acetylene flame to be measured by the thermopile from time to time, produces air currents, set up by local differences in the temperature of the room. The sensitiveness of the whole arrangement was necessarily so great that if the hand was put before the thermopile at the distance of 1 or 2 decimetres, the deflection of the galvanometer was considerable. This difficulty was evaded in the following manner:—

The thermopile was enclosed in a cylinder of thin copper (about 1 millim. thick; the two circular sides of the front and back being made of the same thin copper. In the centre of the front side a circular opening of about 4½ centims. was cut and in this a copper tube of the same diameter (for the quartz plate) was fixed. In the centre of the circular copper plate behind, a thick but very narrow tube (of about 3 or 4 millims. internal diameter) was fixed for the purpose of seeing and directing the thermopile upon the light of the burner. The thermopile was fixed on a piece of

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* Through an accident our thermopile had only 38 junctions.

ebonite in the middle of the air space of the inner cylinder, so that the larger cone should be fully exposed to the light (except a little of the four corners, the whole cone was exposed) and the thermopile everywhere equally removed from the cylinder. To protect the thermopile from moisture, which is especially fatal to its iron wires, a cylinder with calcium chloride was put into the inner cylinder. By means of the tubes in front and behind, the copper cylinder was fixed in another larger copper cylinder, and the space between was filled with 6 or 7 litres of water. Except the small space of the larger tube in the front side, the narrow tube behind and two narrow tubes on the top, filled with Faraday wax, through which the insulated leads from the thermopile were drawn, the inner cylinder was thus enveloped on all sides by a thick layer of water. The outer copper cylinder was entirely covered by very thick sheets of asbestos. In this way any variation of temperature in the inner cylinder was counteracted by the conductivity of the copper sides, surrounded by water, while the thick sheets of asbestos and the large quantity of water between the cylinders made any rapid change of the temperature of the water due to alteration in the temperature of the room impossible.

It was found that if a continuous water current from the main was passed between the two cylinders (even if the current was passed simultaneously in different places between the cylinders as well as between the front and back sides of the cylinder, and the water from the main was used only after half an hour or an hour, when the temperature of the water from the main ought to be constant), very large deflections of the galvanometer, as much as several centimetres, were observed, and these varied continuously though the thermopile was closed to light and should have given no deflection at all. Obviously the temperature of the water from the main is never quite constant, continually varying by several thousandths or even hundredths of a degree Besides this, layers of different temperature may exist in the bulk of the surrounding water owing to the fact that the temperature of water from the main is lower than that of the room, and that it must take a long time before the 6 or 7 litres of water in the cylinders are replaced by fresh water from the main, *i.e.*, the bulk of the water is exposed to the influence of the warmer temperature of the room for a longer time, and this warmer water is being continually mixed with the cold water from the main. This difficulty was finally overcome by leaving the 6 or 7 litres in the cylinders to assume the temperature of the room, giving up the stirring altogether and replacing the same by the water current from the main. Through this the difference between the temperature of the water and that of the room was made very small, *i.e.*, the warming of the water between the cylinders by the surrounding temperature of the room was made exceedingly slow. It should be observed that it is not the constancy of the temperature of the air space of the inner cylinder which we require, but that the variation of its temperature should be the same everywhere, and so slow that it should be in comparison with the velocity of cooling or warming of the thermopile by the surrounding air in the inner cylinder, exceedingly small, while all the junctions should be at the same temperature in the dark.

There still remained other sources of error. In the first instance, there was the quartz plate fixed in front of the larger tube closing up and protecting the inner air space from the air currents of the room. The quartz plate is exposed on the inside to the temperature of the air in the inner cylinder, on the outside to that of the room. There was additional reason why the temperature of the water between the cylinders and of the air space in the inner cylinder had to be brought to the temperature of the room; because it is evidently necessary that the thermopile should be exposed to the same temperature on all sides. In the second instance, the quartz plate and the inner air space between the same, the cone and the copper ring upon which the quartz plate is fixed, are being heated by the rays of light while measurements of the intensity of light are carried out, the rest of the inner cylinder remaining unexposed.

To counteract these sources of error the air space exposed to the light was made very small in comparison with the total air space of the inner cylinder. The narrow circular copper plate (*cp*, fig. 5), on which the quartz plate (*q*) was fixed, was also water-jacketed by means of the india-rubber tube (*y*), so that the four ends of the quartz plate, equal to about one-third of the total surface of the plate, were directly cooled by the narrow circular plate. In front of the quartz plate a large wooden screen was placed, and to its back (not to be seen in this drawing) a copper cylinder was fixed of about 1 inch in thickness and of the same diameter as the outside copper cylinder of the thermopile, filled with water of the same temperature as that contained between the two copper cylinders of the thermopile.

In filling all the apparatus with water from the main, the space between the two copper cylinders was first filled with water through E. From the top of the outer cylinder the water passes through the india-rubber tube (*y*) behind the quartz plates and through the india-rubber tube (*f*) to the lower part of the cylinder which forms the water screen. From the top of the water screen the water passes through an india-rubber tube and pewter pipe (*p*) back to the tank, and then the run of water is stopped. The india-rubber tubes *f* and *y* allow the screen to move up and down, and when it is down the water screen quite covers the whole front surface of the copper cylinder of the thermopile, being removed from it by only about half a centimetre. Direct tests of these arrangements showed them to be successful; after the light has been used and the quartz plates again screened, the deflection returns to the same zero quickly (the thermo-electromotive force in the dark never exceeding about 2 millims.), and remains so for any length of time, and the same deflection is obtained every time the screen is opened again. It takes only a fraction of a minute for the spot of light to attain its maximum deflection or return to zero.

The Galvanometer, &c. (See fig. 7.)

With an acetylene flame of about 250 candle power it was possible to use a Crompton's dead-beat galvanometer instead of the more sensitive one made by Nalder Brothers.

One of the conducting leads *p* from the Rubens thermopile leads to the interrupter E (see diagram p. 357), the purpose of which is either to interrupt the current, or to bring the lead (*p*) from the thermopile into connexion with the lead (*p′*) conducting to the galvanometer (*g*), or to connect the lead (λ) from the nickel-iron thermocouple of the quartz vessel with the lead (*p′*) conducting to the galvanometer. From E the wire passes to the reversing key, which is enclosed in an asbestos box, and from here to the galvanometer (*g*).

The spot of light from an electric incandescent lamp, after passing through a lens, was reflected from the galvanometer mirror upon a transparent celluloid scale.

Great difficulty was experienced in steadying the galvanometer; the suspension of the galvanometer in a box on an india-rubber band, and the placing of the box on a very heavy stone, which again was placed in its turn on thick pieces of india-rubber, gave vibrations of 1 to 2 millims., owing to the fact that the dark room the author had to use was near machinery at work. It was ultimately steadied in the following manner:—A soft thick copper wire was drawn from one wall of the room to the other, and the wire was first stretched and shortened until it stood the weight of the box containing the galvanometer suspended on two very thick and flexible rubber rings. Inside the box the galvanometer (with the wooden plate on which it was standing on pieces of copper) was suspended from one rubber ring on the hook of a screw, which was passed through a hollow wooden cylinder on the top of the wooden box and held by a nut, placed on a metal plate on the top of the wooden cylinder. By raising the screw outside and turning the nut the galvanometer could be brought to any height desired, and by carefully turning the screw it could be placed at any angle, so as to get the spot of light at any required place on the scale. The screws of the galvanometer were resting upon metal pieces on the wooden plate, and adjusted so as to get the required sensitiveness by weakening the magnetic field, *i.e.*, by bringing the circular coil partially out of the central iron core. It was further necessary that the whole arrangement of the suspension of the galvanometer should not be upset by the necessity of fixing the leads to the galvanometer, since it was impossible to ensure that greater vibrations of the leads outside the box would never take place. For this reason the galvanometer was not connected directly with the heavy leads; these were fixed to the wooden box, then for each lead three or four pieces of very thin galvanometer suspension wire (each about 2 inches in length) were soldered to two pieces of thick copper wire; one of them was fixed to the lead and the other to the terminal of the galvanometer. Thus the galvanometer became for the first time quite freely suspended in the box, the fine suspension wires on the one hand allowing free movement to the galvanometer wherever and whenever it may be required, and, on the other hand, exerting no directing influence whatever on its mass.

The small vibrations of the walls of the room were thus allowed to affect the copper wire at the ends, and were weakened almost to zero before they were transmitted to the middle part of the wire. These vibrations in the middle part of the wire were further weakened by the two rubber rings upon which the box with the galvanometer was suspended, and, lastly, the galvanometer itself was made independent both of the vibrations of the box and of the leads. In this way excellent results were obtained, the movements of the spot of light when the scale was removed from the galvanometer 1 or 1·2 metres not exceeding 0·1 millim. Having now, from the acetylene flame, a deflection of the spot of light of about 10 to 15 centims., each reading was brought (and with it the possibility of adjustment of the intensity of light to the right or left) to an accuracy of about 0·1 per cent., an accuracy far greater than that required for the research.

Determination of the Value of the Observed Deflection of the Galvanometer or of the Intensity of Light in Standard Units. (Fig. 7.)

With the arrangement described above, the deflection of the spot of light depends upon conditions which may easily vary according to the circumstance and time. Assuming that the distance of the source of light from the thermopile is fixed, that the flame is in the correct position, that the distance of the scale from the mirror is fixed, still, if the india-rubber rings should become a little stretched in time, or any similar accident happen, the sensitiveness of the galvanometer would vary. It is, therefore, necessary that measurements of the intensity of light should be made independent of variations in the sensitiveness of the galvanometer. It is further desirable to be able to express at once the intensity of light in standard units independently of any given arrangements of the photometer, &c. For this reason, directly after the measurement of the light by means of the thermopile was made, a second measurement was made with a Clark cell and manganin resistances, as given in the above diagram, thus determining the value of the deflection, as caused by the light, in units given by the Clark and manganin resistances.

The Remaining Parts of the Apparatus, &c.

The Bath. (Fig. 5, p. 352.)

The reaction vessel with the mixture of chlorine and hydrogen was immersed in a water-bath and there exposed to light. The bath contained quartz windows, and the reaction vessel was placed behind one of them, the manometer M (E in fig. 1) remaning outside the bath. The volume of the gas in the capillary tubes and in the capillary of the manometer was only a few tenths per cent. of the volume of the gas in the reaction vessel immersed in the bath, so that if the differences between the temperature of the room and that of the bath were very great a small correction was necessary.

Two mercury thermometers were immersed in the bath, one divided into degrees centigrade which could be read to 0°·1, and the other a 0°·1 thermometer of Beckmann's type, with divisions about 3 millims. apart from one another, allowing the temperature of the bath to be read to 0°·01. The thermometers were kept very near to the reaction vessel; the temperature of the gaseous mixture in the reaction vessel with the quartz windows was indicated by the iron-nickel thermocouple inside the same. Later on the temperature was calculated, no thermocouple being employed, to ensure the gaseous mixture not being contaminated with any traces of other substances during the reaction. Near the capillary tube of the manometer was a thermometer, divided into degrees centigrade to indicate the temperature of the room.

To keep the temperature of the bath constant at any desired temperature, the copper bath was large, containing about 70 litres of water. It was covered with very thick sheets of asbestos, placed in a wooden box with an air space between it and the sides of the box, which was placed in another wooden box with another air space between them, while the top of the bath was covered with a wooden lid. At the bottom a small circle was cut out of the wood and asbestos for a rose burner 2 centims. distant from the exposed circle of the copper bottom. The temperature of the bath itself regulated the supply of gas to the burner. The liquid was thoroughly stirred at frequent intervals. Since with all these arrangements the temperature of the bath could not be kept sufficiently constant, owing to the heat absorbed from the powerful acetylene light, the temperature of the bath was adjusted to the desired degree by melting ice, especially when the temperatures required were below 25° or 30°, and by thorough stirring. In this manner the variations of temperature of the bath were kept within as narrow limits as possible during the whole time of the experiment. Each time the readings of the manometer and of the temperature of the bath and of the reaction vessel had to be made, the bath was effectually stirred, readings being taken two minutes later. During this period of two minutes the temperature of the bath near the quartz vessel does not rise under the action of the light more than 0°·01. Since for our purpose it is important to know the difference of the temperature of the gas mixture at two different times, so as to be able to apply the necessary correction, the above manner of making the readings each time two minutes after the bath was well stirred, eliminated the error in the determined differences of temperature almost completely. An investigation of the velocity with which the mercury of the manometer assumes its maximum when the glass bulb or quartz vessel is immersed in the bath showed that after two minutes the temperature of the gas in the bulb is much less than 0°·01 removed from the convergence temperature, the amount of our reading error. This convergence temperature of the gaseous mixture is higher than the temperature of the bath, but always remains constant for the same intensity of the same source of light falling upon the gaseous mixture, provided that the reaction goes on so slowly that the heating of the system by the heat of reaction can be neglected. We are also able from the temperature of the bath to calculate the temperature of the gas mixture. Having once determined the necessary elements for such a calculation (in a manner given by the author on several other occasions)* from the velocity of cooling of the gaseous mixture by the bath and from the velocity of heating of the gaseous mixture by the given source of light (at the beginning of the induction period), a thermocouple was not introduced into the thin glass bulb used instead of the quartz vessel, as it was better to make sure that during the reaction no vapour of any kind could enter into the gaseous mixture from the cement with which the thermocouple has to be fixed in the capillary of the vessel, or from the shellac and pitch with which the wires of the thermocouple have to be covered in order that they may be protected against the action of chlorine. Indeed, the best results, as far as experience goes, were obtained when none of these precautions were neglected.

PART III.

Experimental Results. (Tables I.–V.)

In the following tables the experimental data are given:—

No. is the number of the observation made.

τ is the time at which the observation was made.

$\tau'-\tau''$ is the time between two successive operations.

π is the reading of the manometer E of the quartz vessel at the time τ, read with the cathetometer (38 divisions of the cathetometer scale = 1 millim. of the manometer scale).

$\pi'-\pi''$ is the rise of the manometer E during the time $\tau''-\tau'$.

is the intensity of the acetylene light, *i.e.*, the integral intensity of the light of all wave-lengths contained in the same, expressed in millimetre deflection of the galvanometer read on the scale at the time τ, including the thermo-electromotive force of the Rubens thermopile in the dark; Th.E.M.F. gives the thermo-electromotive force of the Rubens thermopile in the dark, read on the scale at the time τ.

$i'-th.e.m.f'.$ gives the intensity of light at the time τ'. A correction for the deviation of this value from the average intensity of the light during the whole time of the reaction can be applied to the velocity constant K, given in Tables (II., III., IV. and V.), putting K directly proportional to the

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* See "On Real and Apparent Freezing-Points," by M. Wilderman, 'Phil. Mag.,' December, 1897, pp. 474, 475.

intensity of light. I omit, however, this correction, because the variations in the values of K, especially when taken, as in our case, at small intervals, are too considerable for the application of very small corrections to be of any essential use.

Std. gives the sensitiveness of the galvanometer used for the measurement of the intensity of light, measured with standard units (manganin resistances and Clark), and expressed in millimetre deflection of the galvanometer on the same scale. From this the value of (i) is also known in standard units.

t_B is the actual temperature of the bath on 1° thermometer at the time τ.

t_r is the temperature t_B read on the 0°·1 Beckmann thermometer at the same time τ.

$t_{man.}$ is the temperature of the room near the manometer.

Since the volume of the gas in the capillary tubes changes during the reaction, owing to the rise of the mercury in the same, its value is during the reaction from 0·2 per cent. to 0·5 per cent. of the volume of the gas in the quartz vessel or the bulb.

A variation in the temperature of the room = 1° produced a change in the height of the manometer from $\frac{0{\cdot}2 \text{ per cent.}}{273}$ to $\frac{0{\cdot}5 \text{ per cent.}}{273}$ of the total pressure of the gas. When the pressure of the gas = 760 millims., this amounts to $\frac{0{\cdot}2 \times 760}{273 \times 100} = 0{\cdot}005$ millim. to 0·012 millim. per 1° variation in the temperature of the room. So long as we investigate only small intervals of the curve, *i.e.*, when the temperature of the room could not change by 1°, no correction need appear in the tables, and $t_{man.}$ need not enter into the equation. When, however, the curve is investigated at greater time intervals, a correction for $t_{man.}$ can be usefully applied.

$t'_r - t''_r$ is the difference in the temperature of the bath (and gas mixture) at the time τ' and τ'', read to 0°·01 on Beckmann's thermometer.

$t'_r - t''_{r\,corr.}$ is the correction in millimetre pressure, which is to be added to the observed $\pi' - \pi''$ for the variation of the temperature of the bath. This value, when the expansion of the glass bulb is simultaneously accounted for, equals 1·8 millim. for each 1° variation of temperature of the bath. The value of the correction was found from direct observations on the manometer, by bringing the bulb successively to higher temperatures. This correction is especially important when small parts of the curve are investigated, and becomes of smaller importance the greater $\pi' - \pi''$ is, since the variations of t remain almost constant during the whole time of the experiment.

h is the barometric pressure at the time τ, read with the vernier; the temperature of the mercury is given in brackets.

$h'-h''$ is the variation of the barometer on passing from τ' to τ'', when the correction for the temperature of the mercury is also made. This correction must be added to the observed $\pi'-\pi''$; it is for the same day, when the barometer changes very little, of little importance; on the contrary, it becomes important for the ordinary changes of the barometer.

$\pi'-\pi''_{corr.}$ is the true variation in the height of the manometer, if the atmospheric pressure and the temperature of the bath (or of the gas mixture) should have remained constant the whole time, *i.e.*, after the corrections for the variations of the temperature of the bath and for the atmospheric pressure were made. Results were not reduced to normal atmospheric pressure, since this would not serve any purpose (see Table I.).

TABLE I.—CO and Cl_2 (in the glass bulb).

The glass bulb was filled with the gases in the dark. The gases freshly prepared mercury and of the conc. SO_4H_2 (sp.gr. 1·84)) on the manometer was 505·4 millims., temperature of the room 24°·5. On leaving the glass bulb in the dark from Friday, temperature of the room to 22°·3. The manometer rose from 510 to 513·5, *i.e.*, by of barometer and temperature of the room. Thus during three days no combination Barometer, 763·2 (21°·7), temperature of room, 22°·3. Manometer fell to 51·17, *i.e.*, variation of temperature of the room and of the atmospheric pressure. The vessel over the bulb and the temperature of the bath brought the light of the manometer the centre of glass bulb = 62·5 centims.

No.	Time of observation, τ.	$\tau'' - \tau$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+ th.e.m.f.).	i − th. e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection, *std.* (right & left).
1st curve.	h. m.	minutes.		millims.	millims.	millims.	millims.
1	11 50		512·8		—	—	266
		15		0			
2	12 5		512·8		195*	195	—
		45		−0·1 × 2	(th.e.m.f. = 0)		
3	12 50		512·7		—	—	—
		110		−0·3 × 2			
4	2 40		512·4		—	—	—
		80		−0·5 × 2			
5	4 0		511·9		—	—	—
		35		0			
6	4 35		511·9		206	201·5	—
		70		2·6 × 2	(th.e.m.f. = 4·5)		
7	5 45		514·5		—	—	266
Next day	—	—	—	1·3 × 2	—	—	—
2nd curve.							
8	10 33		515·8–364·9		—	—	267
		19		2·3			
9	10 52		517·0–363·8		197	197	—
		10		2·4			
10	11 2		518·3–362·7		—	—	—
		10·5		2·4			

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* At the beginning, during the induction period, when no reaction is visible, no special

Experiment started 5th July, 1901.

in the dark. The partial pressure of Cl_2 (from the variation of the height of the and of CO was 110 millims., when the barometer was 764·6 millims. (21°·7) and the 12 A.M., till Monday, 11 A.M., the barometer changed to 766·85 (21°·4), the (513·5–510·0) 2 = 7 millims. instead of 7·2 millims., which corresponds to the variation whatever took place in the dark. From Monday it was left till Tuesday, 11 A.M. by (51·35–51·17) 2 = 3·6 millims. instead of 3·65 millims., corresponding to the was then placed in the dark of 20°·8. The pressure of the water column in the bath to 512·8. Distance of acetylene light from Rubens' thermopile = 105 centims. ; from

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	1st curve.
20·8	3·47			763·2 (21·4)			1
		0·05*	$1·8 \times 0·05 = 0·09$		0·06	0·15	
—	3·52			—			2
		0·04	$1·8 \times 0·04 = 0·07$		0·17	0·04	
—	3·56			—			3
		0·36	0·65		0·41	0·46 ?	
—	3·92			—			4
		0·43	0·77		0·29	0·06	
—	4·35			—			5
		0·15	0·27		0·13	0·40	
—	4·50			—			6
		0·38	0·68		0·28	6·16	
—	4·88			761·95 (20·8)			7
—	—	−0·48	−0·86	—	−1·8	−0·06	Next day
							2nd curve.
21·7	4·40			763·75 (20·8)			8
		0·03	$1·8 \times 0·03 = 00·5$		0·06	2·41	
—	4·43			—			9
		0·05	0·09		0·03	2·52	
—	4·48			—			10
		0·05	0·09		0·03	2·52	

care was taken to keep the temperature of the bath and the intensity of light constant.

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.		$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+th.e.m.f.).	i − th.e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection, *std.* (right & left).
2nd curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
11	11	12½		519·5–361·5		204 (th.e.m.f. = 2)	202	—
			9·5		2·2			
12	11	22		520·6–360·4		—	—	—
			10·5		2·3			
13	11	32½		521·8–359·3		203 (th.e.m.f. = 2)	201	—
			10		2·0			
14	11	42		522·8–358·3		204 (th.e.m.f. = 2)	202	—
			10		1·9			
15	11	52		523·8–357·4		203·5 (th.e.m.f. = 2)	201·5	—
			10		1·9			
16	12	2		524·7–356·4		—	—	—
			10		1·7			
17	12	12		525·6–355·6		—	—	—
			10		2·3			
18	12	22		526·8–354·5		202 (th.e.m.f. = 2)	200	—
			10		1·5			
19	12	32		527·5–353·7		—	—	—
			10		1·6			
20	12	42		528·3–352·9		—	—	—
			9		1·7			
21	12	51		529·2–352·1		—	—	—
			9·5		1·5			
22	1	2½		530·0–351·4		204 (th.e.m.f. = 2)	201·5	—
			9·5		1·4			
23	1	12		530·7–350·7		—	—	—
			10		1·4			
24	1	22		531·4–350·0		—	—	—
			11·5		2·1			
25	1	33½		532·5–349·0		—	—	—
			8·5		1·1			
26	1	42		533·0–348·4		202 (th.e.m.f. = 3·5)	198·5	—
			10		1·2			
27	1	52		533·6–347·8		—	—	267
			10		1·0			
28	2	2		534·1–347·3		—	—	—
			10		1·4			
29	2	12		534·8–346·6		202 (th.e.m.f. = 3·5)	198·5	—
			10·5		1·3			
30	2	22½		535·5–346·0		202·2 (th.e.m.f. = 3·5)	198·5	—
			11		1·0			
31	2	33½		536·0–345·5		—	—	—
			9		1·2			
32	2	42½		536·6–344·9		—	—	—
			9·5		1·0			

Experiment started 5th July, 1901—(continued).

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	2nd curve.
—	4·53			—			11
		−0·06	−0·11		0·03	2·12	
—	4·47			—			12
		0·05	0·09		0·03	2·42	
—	4·52			—			13
		0·04	0·07		0·03	2·10	
—	4·56			—			14
		−0·03	−0·05		0·03	1·88	
—	4·53			—			15
		0·06	0·11		0·03	2·04	
—	4·59			—			16
		−0·01	−0·02		0·03	1·71	
—	4·58			—			17
		−0·26	−0·47		0·03	1·86	
—	4·32			—			18
		0·04	0·07		0·03	1·60	
—	4·36			—			19
		0·07	0·13		0·03	1·76	
—	4·43			—			20
		−0·15	−0·27		0·03	1·46	
—	4·28			—			21
		0·09	0·16		0·03	1·69	
—	4·37			—			22
		0·05	0·09		0·03	1·52	
—	4·42			763·3 (21·8)			23
		0·06	0·11		0·01	1·52	
—	4·48			—			24
		−0·22	−0·40		0·01	1·71	
—	4·26			—			25
		0·08	0·14		0·01	1·26	
—	4·34			—			26
		0·06	0·11		0·01	1·32	
21·7	4·40			—			27
		0·08	0·14		0·01	1·15	
—	4·48			—			28
		−0·15	−0·27		0·01	1·14	
—	4·33			—			29
		0·05	0·09		0·01	1·40	
—	4·38			—			30
		0·09	1·8 × 0·09 = 0·16		0·01	1·17	
—	4·47			—			31
		−0·14	−0·25		0·01	0·96	
—	4·33			—			32
		0·05	0·09		0·01	1·10	

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.	$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+ th.e.m.f.).	i − th. e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection *std.* (right & left).
2nd curve.	h. m.	minutes.		millims.	millims.	millims.	millims.
33	2 52		537·1–344·4		—	—	—
		11		1·1			
34	3 3		537·7–343·9		—	—	—
		10·5		1·2			
35	3 13½		538·3–343·3		202 (th.e.m.f. = 3·5)	198·5	—
		11		1·0			
36	3 24½		538·8–342·8		—	—	—
		12		1·3			
37	3 36½		539·5–342·2		202 (th.e.m.f. = 3·5)	198·5	—
		13·5		1·1			
38	3 50		540·0–341·6		201 (th.e.m.f. = 3·5)	197·5	—
		16·5		1·6			
39	4 6½		540·8–340·8		202 (th.e.m.f. = 3·5)	198·5	—
		13·5		1·2			
40	4 20		541·4–340·2		204 (th.e.m.f. = 5)	199	—
		15·5		1·1			
41	4 35½		542·0–339·7		—	—	—
		17·0		1·4			
42	4 52½		542·7–339·0		202 (th.e.m.f. = 3·5)	198·5	—
		15		1·0			
43	5 7½		543·3–338·6		203 (th.e.m.f. = 3·5)	199·5	267
		13		1·4			
44	5 20½		544·0–337·9		—	—	—
3rd curve.		11		0·5			
45	5 31½		544·2–337·6		—	—	—
		15		0			
46	5 46½		544·2–337·6		—	—	—
		10		0			
47	5 56½		544·2–337·6		—	—	267
Next day	—	—	—	1·8	—	—	—
4th curve.							
48	10 56		545·0–366·6		202 (th.e.m.f. = 2)	200	265
		10		0			
49	11 6		545·0–336·6		—	—	—
		10		0·4			
50	11 16		545·2–336·4		201 (th.e.m.f. = 1·5)	199·5	—
		10		0·6			

Experiment started 5th July, 1901 (continued).

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	2nd curve.
—	4·38			—			33
		0·09	0·16		0·01	1·27	
—	4·47			—			34
		−0·10	−0·18		0·01	1·03	
—	4·37			—			35
		0·09	0·16		0·01	1·17	
—	4·46			—			36
		−0·11	−0·20		0·02	1·21	
—	4·35			—			37
		0·11	0·20		0·02	1·32	
—	4·46			—			38
		−0·09	−0·16		0·02	1·46	
—	4·37			—			39
		−0·03	−0·05		0·02	1·17	
—	4·34			—			40
		0·12	0·22		0·02	1·34	
—	4·46			—			41
		−0·05	−0·09		0·02	1·33	
—	4·41			—			42
		0·12	0·22		0·02	1·24	
—	4·53			—			43
		−0·16	−0·29		0·02	1·13	
—	4·37			—			44
		0·02	0·04		0·01	0·55	3rd curve.
—	4·39			—			45
		0·07	0·13		0·02	0·15	
—	4·46			—			46
		0·07	0·13		0·01	0·14	
—	4·53			762·85 (21·4)			47
—	—	−0·21	−0·38	—	−1·7	−0·28	Next day
							4th curve.
—	4·32			764·55 (21·4)			48
		0·01	0·02		0·06	0·08	
—	4·33			—			49
		0·03	0·05		0·06	0·51	
—	4·36			—			50
		0·06	0·11		0·06	0·77	

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.		$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+ th.e.m f.).	i − th.e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection *std.* (right & left).
4th curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
51	11	26		545·5–336·1		—	—	—
			13		1·0			
52	11	39		546·0–335·6		203 (th.e.m.f. = 3)	200	—
			21		2·3			
53	12	0		547·2–334·5		—	—	—
			18·5		1·3			
54	12	18½		547·9–333·9		202 (th.e.m.f. = 2)	200	—
			16		1·2			
55	12	34½		548·5–333·3		203·5 (th.e.m.f. = 2)	201·5	—
			15·5		1·0			
56	12	50		549·0–332·8		201·5 (th.e.m.f. = 2)	199·5	—
			15		1·0			
57	1	5		549·5–332·3		—	—	—
			15		1·0			
58	1	20		550·0–331·8		203·5 (th.e.m.f. = 3)	200·5	—
			20		1·2			
59	1	40		550·6–331·2		202·0 (th.e.m.f. = 3·5)	198·5	—
			20		1·4			
60	2	0		551·3–330·5		203·5 (th.e.m.f. = 3)	200·5	—
			21·5		1·1			
61	2	21½		551·9–330·0		204 (th.e.m.f. = 3)	201	—
			21·0		1·2			
62	2	42½		552·5–329·4		—	—	—
			23·5		0·9			
63	3	6		553·0–329·0		202 (th.e.m.f. = 3)	199	—
			44	—	2·1	—	—	—
5th curve.								
64	3	55		554·0–327·9		199·0	199	—
			22		0·8			
65	4	17		554·4–327·5		202 (th.e.m.f. = 2)	200	—
			23		1·0			
66	4	40		554·9–327·0		—	—	—
			20		0·6			
67	5	0		552·2–326·7		203 (th e.m.f. = 2·5)	200·5	—
			23		1·2			
68	5	23		555·8–326·1		202·5 (th e.m.f. = 2·5)	200	—
			22		0·8			
69	5	45		556·2–325·7		202·5 (th.e.m.f. = 2·5)	200	265

Experiment started 5th July, 1901 (continued).

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	4th curve.
—	4·42			—			51
		0·06	0·11		0·08	1·19	
—	4·48			—			52
		−0·26	−0·47		0·12	1·95	
—	4·22			—			53
		0·13	0·23		0·11	1·64	
—	4·35			—			54
		0	0		0·09	1·29	
—	4·35			—			55
		0·05	0·09		0·09	1·18	
21·7	4·40			—			56
		0·06	0·11		0·09	1·20	
—	4·46			763·9 (22·4)			57
		−0·10	−0·18		0·04	0·86	
—	4·36			—			58
		0·11	0·20		0·06	1·46	
—	4·47			—			59
		−0·10	−0·18		0·06	1·28	
—	4·37			—			60
		0·06	0·11		0·06	1·27	
—	4·43			—			61
		−0·07	−0·13		0·06	1·13	
—	4·36			—			62
		0·20	0·36		0·06	1·32	
—	4·56			—			63
—	—	−0·06	−0·11	—	0·13	2·12	
							5th curve.
—	4·50			—			64
		0·13	0·23		0·06	1·09	
—	4·37			—			65
		0	0		0·06	1·06	
—	4·37			—			66
		0·18	0·33		0·06	0·99	
—	4·55			—			67
		−0·13	−0·23		0·06	1·03	
—	4·42			763·1 (22·12)			68
		0·03	0·05		0·06	0·91	
—	4·45			—			69

If we now draw curves, taking the times τ's as abscissæ and the corresponding amount of carbonyl chloride formed (*i.e.*, the π's) as ordinates, then the $\frac{\pi' - \pi''}{\tau_2 - \tau_1}$'s or $\frac{d\pi}{d\tau}$'s give the rate of formation of carbonyl chloride, or the rate of combination of chlorine and carbon monoxide. The curves appear to be remarkably regular, especially those obtained with the glass bulb. The total number of direct observations is in Table I. about 70. To trace the nature of the curve through its whole length observations were made at small intervals, thus dispensing with interpolating results. Errors arising from the variations of the temperature of the bath, from the variations of the barometric pressure, &c., can never be completely eliminated by the application of corrections. For this reason they are greater in the results obtained for small intervals than when greater ones are taken. By this method the phenomenon is nevertheless more thoroughly known and its nature more evident, since such an investigation of the curve does not permit of phenomena characteristic of only one part of the curve obscuring the true nature of other parts of the curve. As will be seen from the tables given below this course proved to be necessary in our case, since at the beginning of the curves we always met with a peculiar phenomenon, called "induction," not characteristic of the rest of the curve.

When the $\frac{\pi' - \pi''}{\tau_2 - \tau_1}$'s or $\frac{d\pi}{d\tau}$'s are successively taken on the curve and compared with one another, we find that they start with very small values approaching zero (the curve starts asymptotically to the abscissa), and gradually increase till they reach a maximum, after which they gradually decrease. If we consider curves (1), (2), (3), (4) and (5) of Table I. as parts of the same curve, belonging all to one system, we find that the $\frac{d\pi}{d\tau}$'s gradually diminish, approaching the value of zero, *i.e.*, when no more reaction takes place. This takes place when one of the combining substances completely disappears from the gas mixture.

An investigation of the curves, after the $\frac{d\pi}{d\tau}$'s arrived almost at their maximum, shows with absolute certainty that the equation

$$[\log_e (A - x_1) - \log_e (A - x_2) + \log_e (B - x_2) - \log_e (B - x_1)] : (\tau_2 - \tau_1) = C \quad (1)$$

(a constant) holds good, where A and B are the quantities or volumes or partial pressures of chlorine and carbon monoxide before the reaction was first started, expressed in millimetre pressure of the manometer. $A - x_1$, $A - x_2$, $B - x_1$, $B - x_2$, are the quantities of chlorine and of carbon monoxide present in the system at the times τ_1 and τ_2 (see Table II. below).

It is thus evident that our integral equation must be

$$\frac{1}{A-B}[\log_e (A - x_1) - \log_e (A - x_2) + \log_e (B - x_2) - \log_e (B - x_1)] : (\tau_2 - \tau_1) = K \quad (2).$$

The differential equation giving the law of velocity of reaction is thus

$$\frac{dx}{d\tau} = \mathrm{K}\,(\mathrm{A} - x)\,(\mathrm{B} - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

i.e., the velocity of combination of chlorine and carbon monoxide in light, or the velocity of the formation of carbonyl chloride, is at the time τ directly proportional to the product of the reacting masses at the time τ. Since the chemical equation for the reaction is $Cl_2 + CO = COCl_2$, this equation in light has the form which it ought to have according to the law of mass action in homogeneous systems, if the chemical reaction were to go on in the dark as the outcome of those intrinsic properties of matter only, which we call chemical affinity or chemical potential. In the above equations K is the velocity constant, which gives the velocity of combination of chlorine and carbon monoxide under given conditions of experiment, when $\mathrm{A} - x$ for chlorine is 1 and $\mathrm{B} - x$ for carbon monoxide is 1. K in the above equations is evidently also an integral velocity constant for all wave lengths of the acetylene light, the value of (K) being different for each wave length. Since, however, each wave length has an equation of the same form $\frac{dx}{d\tau} = (\mathrm{K})\,(\mathrm{A} - x)\,(\mathrm{B} - x)$, the equation for light consisting of more than one wave length remains the same; K or (K) is besides a function of the intensity of light, of the temperature, and of the surrounding medium.

In the following tables (II., III., IV. and V.):

No. is the number of the observation.

$\pi' - \pi'' = dx$ is the amount of carbonyl chloride formed, or of chlorine or of carbon monoxide which has disappeared during the times $\tau_2 - \tau_1$.

$\mathrm{A} - x$ is the quantity of chlorine present in the system at the time τ.

$\mathrm{B} - x$ is the quantity of carbon monoxide present in the system at the time τ.

$\tau_2 - \tau_1$ is the time between two successive observations.

Equation (2) should be true if the law of mass action holds good.

$\frac{dx}{d\tau}$ gives the rate of formation of carbonyl chloride at the successive times; this ought to be constant, if the rate of formation of carbonyl chloride in a unit of time were independent of the reacting masses and were directly proportional to the intensity of the light introduced only.

$\frac{dx}{d\tau} : (\mathrm{A} - x)$ gives the rate of formation of carbonyl chloride at the time τ, divided by the quantity of chlorine present in the system at the time τ. This ought to be constant if the rate of formation of carbonyl chloride at a given intensity of light were directly proportional to the amount of light absorbed by the system (*i.e.*, by chlorine) in the unit of time during the reaction.

TABLE II.—Cl_2 and CO (in the Glass Bulb). Experiment started 5th July, 1901. Temperature ca. 21°·7.

No.	$\pi' - \pi''$ $= dx$.	$A - x$ (Cl_2).	log ($A - x$).	log ($A - x_1$) $-$ log ($A - x_2$).	$B - x$ (CO).	log ($B - x$).	log ($B - x_1$) $-$ log ($B - x_2$).	Σ log = [log ($A - x_1$) $-$ log ($A - x_2$)] $-$ [log ($B - x_1$) $-$ log ($B - x_2$)].	$\tau_2 - \tau_1$.	$\frac{\Sigma \log}{\tau_2 - \tau_1} . 10^4$ $= (A - B) K \times 10^4 : 2·3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^6}$.	K . 10^7 : 2·3026.
1st curve.									minutes.				
1		502·4	2·70105		109·4	2·03902							
	0·15			·00013			·00060	·00047	15	0·31	1·0	20	0·79
2		502·25	2·70092		109·25	2·03842							
	0·04			·00003			·00016	·00013	45	0·029	0·1	2	0·07
3		502·21	2·70089		109·21	2·03826							
	0·46 ?			·00041 ?			·00183 ?	·00142 ?	110	0·13 ?	0·4	8	0·33
4		501·75	2·70048		108·75	2·03643							
	0·06			·00004			·00024	·00020	80	0·025	0·07	14	0·06
5		501·69	2·70044		108·69	2·03619							
	0·40			·00035			·00160	·00125	35	0·357	1·1	22	0·91
6		501·29	2·70009		108·29	2·03459							
	6·16			·00537			·02543	·02006	70	2·87	8·8	177	7·30
7		495·13	2·69472		102·13	2·00916							
Next day.	$-$0·06												
2nd curve.													
8		495·19	2·69477		102·19	2·00941							
	2·41			·00212			·01037	·00825	19	4·34	12·7	256	11·04
9		492·78	2·69265		99·78	1·99904							
	2·52			·00223			·01111	·00888	10	8·88	25·2	509	22·59
10		490·26	2·69042		97·26	1·98793							
	2·52			·00223			·01140	·00917	10·5	8·73	24·0	492	22·21
11		487·74	2·68819		94·74	1·97653							
	2·12			·00189			·00983	·00794	9·5	8·36	22·3	459	21·27
12		485·62	2·68630		92·62	1·96670							
	2·42			·00217			·01149	·00932	10·5	8·87	23·0	476	22·56
13		483·20	2·68413		90·20	1·95521							
	2·10			·00189			·01023	·00834	10	8·34	21·0	437	21·22
14		481·10	2·68224		88·10	1·94498							
	1·88			·00170			·00937	·00767	10	7·67	18·8	392	19·51
15		479·22	2·68054		86·22	1·93561							
	2·04			·00186			·01040	·00854	10	8·54	20·4	427	21·72

16		477·18	2·67868		84·18	1·92521							
	1·71			·00156			·00891	·00735	10	7·35	17·1	360	18·70
17		475·47	2·67712		82·47	1·91630							
	1·86			·00170			·00991	·00821	10	8·21	18·6	393	20·88
18		473·61	2·67542		80·61	1·90639							
	1·60			·00147			·00871	·00724	10	7·24	16·0	339	18·42
19		472·01	2·67395		79·01	1·89768							
	1·76			·00162			·00978	·00816	10	8·16	17·6	374	20·76
20		470·25	2·67233		77·25	1·88790							
	1·46			·00135			·00829	·00694	9	7·77	16·2	345	19·76
21		468·79	2·67098		75·79	1·87961							
	1·69			·00157			·00979	·00822	9·5	8·65	17·8	381	22·00
22		467·10	2·66941		74·10	1·86982							
	1·52			·00142			·00900	·00758	9·5	7·98	16·0	344	20·30
23		465·58	2·66799		72·58	1·86082							
	1·52			·00142			·00919	·00777	10	7·77	15·2	327	19·77
24		464·06	2·66657		71·06	1·85163							
	1·71			·00160			·01058	·00898	11·5	7·81	14·9	322	19·87
25		462·35	2·66497		69·35	1·84105							
	1·26			·00118			·00797	·00679	8·5	7·99	14·8	320	20·33
26		461·09	2·66379		68·09	1·83308							
	1·32			·00125			·00850	·00725	10	7·25	13·2	287	18·45
27		459·77	2·66254		66·77	1·82458							
	1·15			·00109			·00754	·00645	10	6·45	11·5	251	16·41
28		458·62	2·66145		65·62	1·81704							
	1·14			·00108			·00761	·00653	10	6·53	11·4	249	16·61
29		457·48	2·66037		64·48	1·80943							
	1·40			·00133			·00954	·00821	10·5	7·82	13·3	291	19·90
30		456·08	2·65904		63·08	1·79989							
	1·17			·00111			·00813	·00702	11	6·38	10·6	233	16·23
31		454·91	2·65793		61·91	1·79176							
	0·96			·00092			·00679	·00587	9	6·52	10·7	235	16·59
32		453·95	2·65701		60·95	1·78497							
	1·10			·00106			·00791	·00685	9·5	7·21	11·5	255	18·34
33		452·85	2·65595		59·85	1·77706							
	1·27			·00122			·00931	·00809	11	7·35	11·5	254	18·70
34		451·58	2·65473		58·58	1·76775							
	1·03			·00099			·00770	·00671	10·5	6·41	9·8	217	16·30
35		450·55	2·65374		57·55	1·76005							
	1·17			·00113			·00892	·00779	11	7·08	10·6	236	18·01
36		449·38	2·65261		56·38	1·75113							
	1·11			·00107			·00864	·00757	12	6·31	9·2	205	16·05
37		448·27	2·65154		55·27	1·74249							
	1·32			·00128			·01050	·00922	13·5	6·83	9·8	219	17·38

TABLE II.—Cl_2 and CO (in the Glass Bulb). Experiment started 5th July, 1901. Temperature ca. 21°·7 (continued).

No.	$\pi' - \pi'' = dx$.	$A-x$ (Cl_2).	log ($A-x$).	log ($A-x_1$) $-$log ($A-x_2$).	$B-x$ (CO).	log ($B-x$).	log ($B-x_1$) $-$log ($B-x_2$).	$\Sigma \log =$ [log ($A-x_1$) $-$ log ($A-x_2$)] $-$ [log ($B-x_1$) $-$ log ($B-x_2$)].	$\tau_2-\tau_1$.	$\frac{\Sigma \log}{\tau_2-\tau_1} . 10^4$ $=(A-B) K \times 10^4 : 2·3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A-x}{10^6}$.	$K . 10^7 : 2·3026$.
									minutes.				
38		446·95	2·65026		53·95	1·73199							
	1·46			·00142			·01191	·01049	16·5	6·36	8·8	197	16·18
39		445·49	2·64884		52·49	1·72008							
	1·17			·00114			·00979	·00865	13·5	6·48	8·7	191	16·49
40		444·32	2·64770		51·32	1·71029							
	1·34			·00132			·01149	·01017	15·5	6·56	8·9	201	16·69
41		442·98	2·64638		49·98	1·69880							
	1·33			·00130			·01172	·01042	17	6·13?	7·6	172	15·60
42		441·65	2·64508		48·65	1·68708							
	1·24			·00122			·01121	·00999	15	6·66	8·3	188	16·95
43		440·41	2·64386		47·41	1·67587							
	1·13			·00112			·01048	·00936	13	7·20	8·7	198	18·32
44		439·28	2·64274		46·28	1·66539							
	0·55			·00054			·00519	·00465	11	7·23	5·0	114	10·75
3rd curve. 45		438·73	2·64220		45·73	1·66020							
	0·15			·00015			·00143	·00128	15	0·85	1·0	23	2·16
46		438·58	2·64205		45·58	1·65877							
	0·14			·00014			·00133	·00119	10	1·19	1·4	32	3·03
47		438·44	2·64191		45·44	1·65744							
Next day.	−0·28												
4th curve. 48		438·72	2·64219		45·72	1·66011							
	0·08			·00008			·00076	·00068	10	0·68	0·8	18	1·73
49		438·64	2·64211		45·64	1·65935							
	0·51			·00051			·00488	·00437	10	4·37	5·1	116	11·10
50		438·13	2·64160		45·13	1·65447							
	0·77			·00076			·00748	·00672	10	6·72	7·7	176	17·10
51		437·36	2·64084		44·36	1·64699							
	1·19			·00118			·01181	·01063	13	8·58	9·1	208	21·83

52	1·95	436·17	2·63966	·00195	43·17	1·63518	·02007	·01812	21	8·63	9·3	214	21·93
53	1·64	434·22	2·63771	·00164	41·22	1·61511	·01763	·01599	18·5	8·64	8·8	203	21·98
54	1·29	432·58	2·63607	·00130	39·58	1·59748	·01439	·01309	16	8·18	8·1	188	20·80
55	1·18	431·29	2·63477	·00119	38·29	1·58309	·01360	·01241	15·5	8·00	7·6	176	20·35
56	1·20	430·11	2·63358	·00121	37·11	1·56949	·01427	·01306	15	8·70	8·0	186	22·14
57	0·86	428·91	2·63237	·00088	35·91	1·55522	·01053	·00965	15	6·43	5·7	133	16·44
58	1·46	428·05	2·63149	·00148	35·05	1·54469	·01848	·01700	20	8·50	7·3	171	21·62
59	1·28	426·59	2·63001	·00130	33·59	1·52621	·01687	·01557	20	7·78	6·4	151	19·80
60	1·27	425·31	2·62871	·00130	32·31	1·50934	·01742	·01612	21·5	7·50	5·9	139	19·08
61	1·13	424·04	2·62741	·00116	31·04	1·49192	·01610	·01494	21·0	7·11	5·4	128	18·09
62	1·32	422·91	2·62625	·00136	29·91	1·47582	·01961	·01825	23·5	7·76	5·6	133	19·74
63		421·59	2·62489		28·59	1·45621							
	2·34			·00242			·03708	·02466	44	5·60	5·3	126	14·25
5th curve. 64	1·09	419·25	2·62247	·00113	26·25	1·41913	·01842	·01729	22	7·86	5·0	120	20·00
65	1·06	418·16	2·62134	·00110	25·16	1·40071	·01869	·01759	23	7·65	4·6	110	19·46
66	0·99	417·10	2·62024	·00103	24·10	1·38202	·01822	·01719	20	8·59	4·9	118	21·85
67	1·03	416·11	2·61921	·00108	23·11	1·36380	·01988	·01880	23	8·17	4·7	113	20·79
68	0·91	415·08	2·61813	·00095	22·08	1·34400	·01828	·01733	22	7·88	4·1	99	20·05
69		414·17	2·61718		21·17	1·32572							

The amount transformed into $CO.Cl_2 = \frac{88\cdot23}{109\cdot40} = 80\cdot65$ per cent.

TABLE III.—CO and Cl_2 (Quartz Vessel). Started 13th December, 1900. Temperature of Bath 43°·7 C.

Distance of acetylene light from Rubens thermopile = 105 centims., from the centre of quartz vessel = 66·5 centims

The quantity of Cl_2 taken was 224·7 millims. (at 43°·7); of CO, 343·6 millims. (at 43°·7).

The resistance D connected with the galvanometer of diagram (fig. 7, p. 357) was in this case 1 ohm instead of 6 ohms; the sensitiveness of the galvanometer was then right and left = 461 millims. The intensity of the light, removed by the same distance of 105 centims. from the thermopile, was right and left: (1)–(2) 190·4, (2)–(3) 194·5, (3)–(4) 194·5, (4)–(5) 192·5, (5)–(6) 192·5, (6)–(7) 195, (7)–(8) 195. The light intensity was kept more carefully constant on the second day: (9)–(10) 193·5, (10)–(11) 193·5, (11)–(12) 194·5, (12)–(13) 193·5, (13)–(14) 193·5, (14)–(15) 193·5. The temperature of the bath was, except (3), when it was 43°·95, always 43°·7. It was easier to keep the bath constant at this temperature. The variation of the barometer (759 millims.) was very small and could be neglected.

No.	$\pi'-\pi''=dx$.	$A-x$ (Cl_2).	log ($A-x$).	log ($A-x_1$) −log ($A-x_2$).	$B-x$ (CO).	log ($B-x$).	log ($B-x_1$) − log ($B-x_2$).	$-\Sigma\log = -$ −[log ($A-x_1$) −log ($A-x_2$)] +[log ($B-x_1$) −log ($B-x_2$)].	$\tau_2-\tau_1$.	$\frac{-\Sigma\log}{\tau_2-\tau_1}.10^5$ $=(B-A)K\times 10^5:2\cdot3026$.	$\frac{dx}{d\tau}.100$.	$\frac{dx}{d\tau}:\frac{A-x}{10^5}$.	$K.10^7:2\cdot3026$.
									minutes.				
1		224·7	2·35160		343·6	2·53605							
	0			0			0	0	85	0	0		0
2		224·7	2·35160		343·6	2·53605							
	3·0 × 2			·01175			·00765	·00410	25	16·4	24·0	110	13·8
3		218·7	2·33985		337·6	2·52840							
	2·0 × 2			·00802			·00517	·00285	17	16·7	23·5	110	14·0
4		214·7	2·33183		333·6	2·52323							
	3·5 × 2			·01439			·00921	·00518	18	28·8	38·9	187	24·2
5		207·7	2·31744		326·6	2·51402							
	2·5 × 2			·01059			·00670	·00389	15	25·8	33·3	164	21·7
6		202·7	2·30685		321·6	2·50732							
	4·0 × 2			·01748			·01094	·00654	20	32·7	40·0	205	27·5

7		194·7	2·28937		313·6	2·49638							
	1·0 × 2			·00449			·00278	·00171	6	28·5	33·3	173	24·0
8		192·7	2·28488		311·6	2·49360							
Next day	(barometer 766 millims.).												
9		185·7	2·26881		304·6	2·48373							
	7·5 × 2			·03658			·02193	·01465	83	17·6	18·0	105	14·8
10		170·7	2·23223		289·6	2·46180							
	4·0 × 2			·02084			·01217	·00867	30	28·9	26·6	163	24·3
11		162·7	2·21139		281·6	2·44963							
	4·1 × 2			·02246			·01283	·00963	30	30·8	27·3	177	25·9
12		154·5	2·18893		273·4	2·43680							
	3·1 × 2			·01779			·00996	·00783	30	26·1	20·6	139	22·0
13		148·3	2·17114		267·2	2·42684							
	3·0 × 2			·01794			·00987	·00807	30	26·9	20·0	140	22·6
14		142·3	2·15320		261·2	2·41697							
	2·8 × 2			·01743			·00941	·00802	30	26·7	18·6	136	22·5
15		136·7	2·13577		255·6	2·40756							

The total amount transformed into $CO.Cl_2$ is $\frac{88}{224 \cdot 7} = 39 \cdot 16$ per cent.

TABLE IV.—CO and Cl_2 (Quartz Vessel). Started 13th December, 1900. Temperature of Bath 43°·7.

Distance of the acetylene light from thermopile = 105 centims., from the centre of the quartz vessel = 62·5 centims. The quantity of Cl_2 taken was 287·8 millims. (43°·7); of CO, was 359·4 millims. (at 43°·7). Barometer, 759 millims. The sensitiveness of the galvanometer, temperature of bath, atmospheric pressure, &c., were here the same as in Table (III.).

The Cl_2 and CO are absolutely the same as in Table III.; only exceedingly small traces of air could enter the gas mixture from the conc. SO_4H_2, with which the Cl_2 gas was pressed into the quartz vessel.

No.	$\pi' - \pi'' = dx$.	A − x (Cl_2).	log (A − x).	log (A − x_1) − log (A − x_2).	B − x (CO).	log (B − x).	log (B − x_1) − log (B − x_2).	− Σ log = − [log (A − x_1) − log (A − x_2)] + [log (B − x_1) − log (B − x_2)].	$\tau_2 - \tau_1$.	$\frac{-\Sigma \log}{\tau_2 - \tau_1} . 10^5 = (B - A) K \times 10^5 : 2·3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^5}$.	K . 10^7 : 2·3026.
									minutes.				
1		287·8	2·45909		359·4	2·55558							
	0			0			0	0	85	*	*	*	*
2		287·8	2·45909		359·4	2·55558							
	2·0 ?			·00303			·00243	·00060	25	2·4 ?	8·00 ?	28·0 ?	3·35 ?
3		285·8	2·45606		357·4	2·55315							
4	1·6			·00244			·00194	·00050	35	1·43	4·57	16·1	2·00
5		284·2	2·45362		355·8	2·55121							
	1·0			·00153			·00123	·00030	15	2·00	6·66	23·5	2·79
6		283·2	2·45209		354·8	2·54998							
	1·0			·00153			·00122	·00031	20	1·55	5·00	17·7	2·17
7		282·2	2·45056		353·8	2·54876							
Next day.													
8		282·2	2·45056		353·8	2·54876							
	1·0			·00154			·00123	·00031	83	·37	1·20	4·27	·52
9		281·2	2·44902		352·8	2·54753							
	2·0			·00310			·00247	·00063	30	2·10	6·66	23·9	2·98
10		279·2	2·44592		350·8	2·54506							
	3·0			·00470			·00363	·00107	30	3·56	10·00	36·2	4·97
11		276·2	2·44122		347·8	2·54133							
	3·0			·00474			·00376	·00098	30	3·27	10·00	36·6	4·57
12		273·2	2·43648		344·8	2·53757							
	3·0			·00479			·00380	·00099	30	3·30	10·00	37·0	4·61
13		270·2	2·43169		341·8	2·53377							

* The total amount transformed into $CO.Cl_2$ is $\frac{17·6}{287·8} = 6·11$ per cent. It is evident that with such small variations in the masses of the reacting substances, none of the last four columns can show in preference to the others which is the fundamental law underlying the phenomena of velocity of reaction.

TABLE V.—CO and Cl_2 (in the Glass Bulb), 21st July, 1901.

Distance of the acetylene light from Rubens thermopile = 105 centim., from the centre of the glass bulb = 62·5 centims.

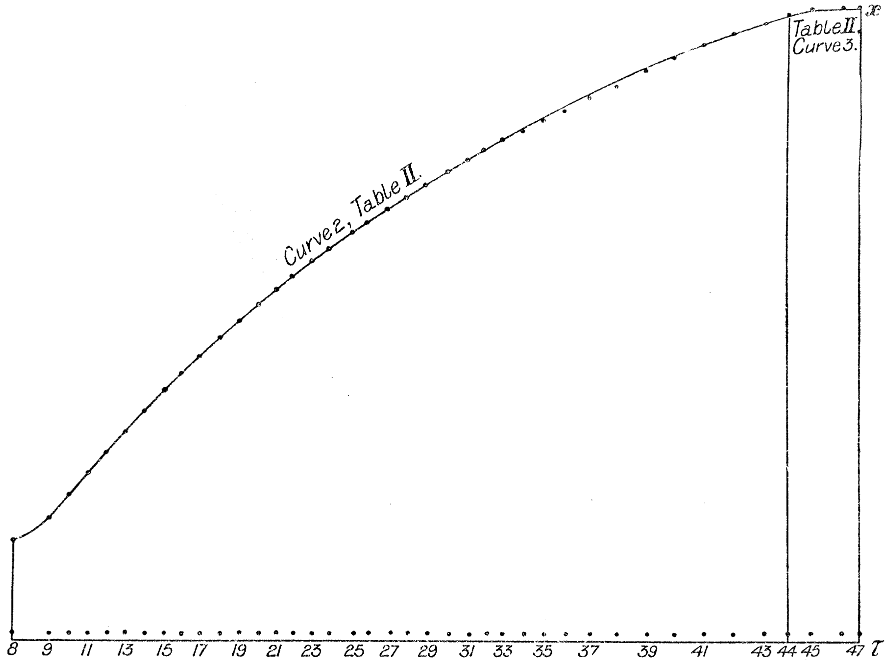
The quantity of Cl_2 = 388·27 millims. (at 21°·3 and 757·85 (22°·9) barometer pressure), the quantity of CO = 350·68 millims. The gases the same as in curves 1, 2, 3, 4, 5, only the CO dried by a longer column of conc. SO_4H_2. The intensity of light was: (1)–(2) 202·5, (2)–(3) 202·0, (3)–(4) 201 to 202, (4)–(5) 201–202, (5)–(6) 201–202, (7)–(8) 202, (8)–(9) 202–202·5, (9)–(10) 202, (10)–(11) 202, (11)–(12) 202, (12)–(13) 201, (13)–(14) 201, (14)–(15) 201, (15)–(16) 201, (16)–(17) 201, (17)–(18) 201. Calibration, as in curves 1, 2, 3, 4, 5 = 263 millims. (r and l). Barometer, 757·85 (22°·9), fell to 756·35 (22°·7).

No.	$\pi'-\pi''$ $=dx$.	$A-x$ (Cl_2).	log ($A-x$).	log ($A-x_1$) $-$log ($A-x_2$).	$B-x$ (CO).	log ($B-x$).	log ($B-x_1$) $-$log ($B-x_2$).	Σ log = [log ($A-x_1$) $-$ log ($A-x_2$)] $-$ [log ($B-x_1$) $-$ log ($B-x_2$)].	$\tau_2-\tau_1$.	$\frac{\Sigma \log}{\tau_2-\tau_1}.10^6$ $=(A-B)K\times 10^6:2\cdot3026$.	$\frac{dx}{d\tau}.100$.	$\frac{dx}{d\tau}:\frac{A-x}{10^5}$.	K . 10^7 : 2·3026.
									minutes.				
1		388·27	2·58915		350·68	2·54491							
	0			0			0	0	47	0	0	0	0
2		388·27	2·58915		350·68	2·54491							
	−0·02			0			0	0	48	0	0	0	0
3		388·29	2·58916		350·70	2·54494							
	0·17			·00020			·00021	·00001	149	·07	·011	0·03	·02
4		388·12	2·58896		350·53	2·54473							
	0·51			·00057			·00063	·00006	69	·87	0·74	1·91	·20
5		387·61	2·58839		350·02	2·54410							
	1·02			·00114			·00127	·00013	24	5·42	4·25	11·0	1·44
6		386·59	2·58725		349·00	2·54283							
Next day, 750·40 (21°·7), barometer fell to 748·55 (21°·85) at 18); risen after the interruption of light by 0·8 millim. (calculated).													
7		385·79	2·58635		348·20	2·54183							
	12			·00013			·00015	·00002	12	1·67	1·00	2·59	·44
8		385·67	2·58622		348·08	2·54168							
	3·03			·00344			·00380	·00036	47	7·66	6·45	16·86	2·04

TABLE V.—CO and Cl_2 (in the Glass Bulb), 21st July, 1901—continued.

No.	$\pi'-\pi''$ $=dx$.	$A-x$ (Cl_2).	log $(A-x)$.	$\log(A-x_1)$ $-\log(A-x_2)$.	$B-x$ (CO).	log $(B-x)$.	$\log(B-x_1)$ $-\log$ $(B-x_2)$.	$\Sigma\log=$ $[\log(A-x_1)$ $-\log(A-x_2)]$ $-[\log(B-x_1)$ $-\log(B-x_2)]$.	$\tau_2-\tau_1$.	$\frac{\Sigma\log}{\tau_2-\tau_1}.10^6$ $=(A-B)K\times$ $10^6:2\cdot3026$.	$\frac{dx}{d\tau}.100$.	$\frac{dx}{d\tau}:\frac{A-x}{10^5}$.	$K.10^7:$ $2\cdot3026$.
									minutes.				
9		382·64	2·58278		345·05	2·53788							
	3·48			·00396			·00440	·00044	40·5	10·87	8·59	22·66	2·89
10		379·16	2·57882		341·57	2·53348							
	2·38			·00272			·00303	·00031	19·5	15·90	12·20	32·40	4·23
11		376·78	2·57610		339·19	2·53045							
	3·19			·00371			·00411	·00040	28	14·29	11·40	30·50	3·80
12		373·59	2·57239		336·00	2·52634							
	3·55			·00414			·00461	·00047	30	15·67	11·84	31·96	4·17
13		370·04	2·56825		332·45	2·52173							
	3·45			·00408			·00453	·00045	30	15·00	11·50	31·42	4·00
14		366·59	2·56417		329·00	2·51720							
	1·99			·00235			·00264	·00029	16	18·13	12·44	34·10	4·82
15		364·60	2·56182		327·01	2·51456							
	3·13			·00375			·00418	·00043	25	17·20	12·52	34·60	4·57
16		361·47	2·55807		323·88	2·51038							
	1·79			·00215			·00240	·00025	15	16·67	11·94	33·20	4·43
17		359·68	2·55592		322·09	2·50798							
	1·64			·00199			·00222	·00023	15	15·33	10·94	30·56	4·08
18		358·04	2·55393		320·45	2·50576							

The total amount transformed into $CO.Cl_2=\frac{29\cdot51}{350\cdot68}=8\cdot41$ per cent.


Curve 2, Table II.
Table II.
Curve 3.
x
8
9
11
13
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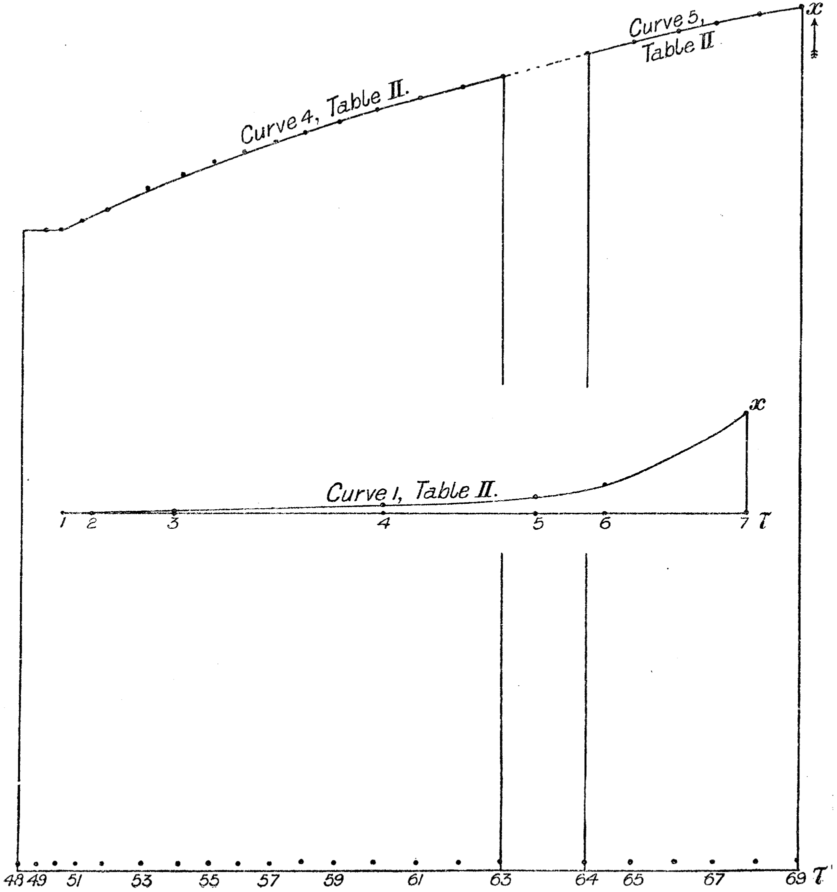
Curve 5, Table II
x
Curve 4, Table II.
Curve 1, Table II.
x
1
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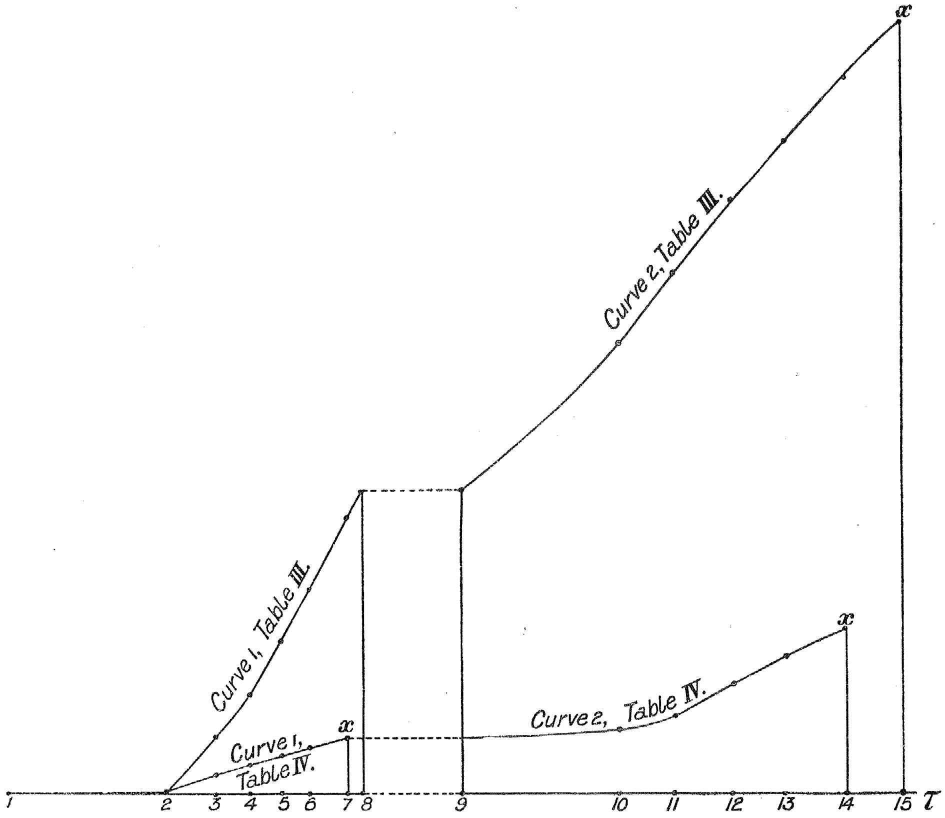

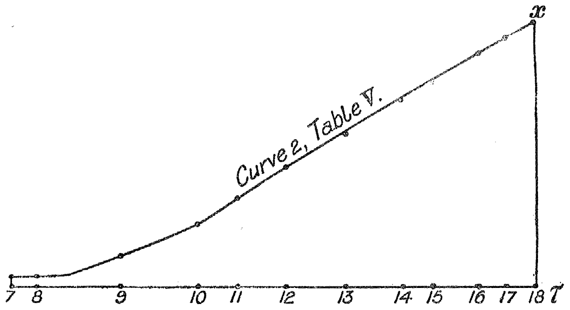

In the above tables curves (1), (2), (3), (4), and (5), all belong to one system at 21°·7.

The values of K in the above tables, calculated from equation (1), show, that as the system is brought from the dark to the light the reaction at first does not appear to be going on, then it goes on very slowly giving very small values for K, gradually the values for K, and with it the speed of reaction, increase until the values obtained for K remain constant, the speed diminishing at the same time according to the law of mass action. If after the values of K remain constant for a sufficient time, the light is removed for some hours, and the system again exposed to the light, we again find the same phenomenon ; the velocity constant K is not obtained at once but only after the reaction has gone on for some time. Further, it is found that in every case the same velocity constant is obtained after a time. It follows from this that the combining chlorine and carbon monoxide when exposed to light of a certain intensity and composition, always acquire after a certain time the same constant properties, the same chemical affinity to one another. The fact that the same constant was found in all curves of the same system, and that the investigation was carried on as far as 80·66 per cent. (in Tables I. and II.) and 39·16 per cent. (in Table III.) of the total amount of possible combination, shows that the above equation (3), p. 377, which is a true expression of the law of mass action, truly represents the fundamental law underlying chemical kinetics in light. At the same time the last two columns of the above tables illustrate beyond any doubt that it is no longer possible to assume that a law analogous to FARADAY'S for electrolysis governs the phenomena of chemical kinetics in light.

Instead of getting a constant in the last columns, the values of $dx/d\tau \cdot 100$ fall from 25·2 to 4·1 (in Table II.), and from 40 to 18·6 (in Table III.), and the values of $\frac{dx}{d\tau} : \frac{(\mathrm{A} - x)}{10^5}$ (in Table II.) fall from 50·9 to 9·9, and (in Table III.) from 205 to 136. Special attention should be given to the curves (1), (2), (3), (4), and (5), of Table II. Here a large quantity of chlorine and a small quantity of carbon monoxide were employed ; in this way the variations in the quantity of carbon monoxide were increased, and in that of chlorine made small, *i.e.*, it is the variation in the quantity of the carbon monoxide which absorbs but little light, and not in the quantity of the chlorine, which absorbs much, which in this case proves to be the main cause of the velocity of reaction decreasing so rapidly. It is thus evident that it is not the quantity of light absorbed by the molecules in the unit of time, but the quantity of the reacting substances present, which determines the velocity of the reaction, no matter what quantity of light the molecules absorb, provided that under the action of light the atoms and molecules acquire that quantity of energy which is characteristic of them after the period of "induction" has passed. In other words a system containing two molecules chlorine and one molecule carbon monoxide will combine at the same rate as a system containing one molecule chlorine and two molecules carbon monoxide, though the first system absorbs almost twice as much light as the second.

The "Induction" and "Deduction" Periods of Energy of the System and the Chemical Periods of "Induction" and "Deduction" in Light.

Having considered those parts of the curves where the velocity constant can be traced, we now consider the parts before the velocity constant is reached. We find that, starting with a system such as chlorine and carbon monoxide, at first it seems for some time that no combination takes place at all. Combination, however, becomes gradually more and more apparent, the velocity becomes greater and greater, till a constant value for K is obtained. This is a peculiar phenomenon, which BUNSEN and ROSCOE first observed in the case of chlorine and hydrogen, and which they appropriately called the "induction period." If now, after the velocity constant has been observed for some time, the light is removed from the system, the reaction at once becomes very slow and soon stops. If the system is, after a time, again exposed to light, we find at first an "induction period," after which the same velocity constant is obtained. This shows that as the light is removed from the system the reacting molecules lose the properties which they had acquired in the light, gradually returning to their old state; and that when the system is again exposed to the light the molecules and atoms each time gradually acquire the same new properties. Besides the "induction period" we thus have to deal also with a "deduction period." The "induction period" is evidently not due to the absence of some product of the reaction, but is a period during which the molecules and atoms of the systems continuously change their state of energy from that in the dark to that in the light; and the "deduction period" is a period during which the molecules and atoms gradually return from their state of energy in the light to the state of energy they possess in the dark. The properties of the "induction" and "deduction" periods require, however, still further consideration. On removing the light from the system, that state of energy of the atoms and molecules which makes them capable of entering into reaction rapidly passes away, with the energy stored in the molecules and atoms under the action of light, and is transformed partly into heat and partly in chemical action as long as this goes on after the removal of the light.

The curves given above show, however, that while chemical action ceases, or apparently ceases, after a short time, it takes a considerable time before the atoms and molecules again completely acquire the properties which they previously had in the dark. Thus, between the first curve and the second (between 7 and 8) the light was removed for 16 hours and 48 minutes, between the third and fourth (between 47 and 48) for 17 hours, between the fourth and fifth (63 and 64) the light was interrupted only for 5 minutes, and the rest of the time (39 minutes) it was again exposed to the light. We nevertheless find that, after 17 hours, the "induction period" of the second curve did not again become as slow as it was in the first curve; after the third interruption of the light, for about the same 17 hours, the "induction period" was almost quite the same—starting with almost the same values of K; again, during the fourth interruption of the light for only a few minutes, the chlorine and carbon monoxide of the system returned only so little to the properties which they had at first in the dark that no marked variation in the value of the velocity constant K could be established. Thus we find a remarkable analogy (though not a reversible identity) between the period of "deduction" and "induction." On exposing the system for the first time to light, the energy of the light is absorbed by the system for a considerable time before the atoms and molecules acquire the state of energy when the reaction becomes apparent, *i.e.*, the energy of the system first continuously increases and changes though no chemical effect can be perceived in the system. When the chemical reaction becomes evident the chemical "induction period" then continues till the new constant state of energy characterised by K is reached. On removing the light, the chemical "deduction period" continues only a short time, when the reaction ceases to take place, but it takes a long time for the atoms and molecules to lose those properties which they acquired in the light before chemical reaction started, and this gradual diminution of the energy of the system is again not to be discovered from the chemical reactions of the systems. The chemical "deduction period," however, lasts much less time than the chemical "induction period." It is evident that the curves of the "induction" and "deduction periods" given above only represent the amount of chemical transformation, *i.e.*, are curves of chemical "induction" and "deduction," and are not the curves which represent the gradual increase and decrease, the "induction" and "deduction" periods, of the whole energy of the system, when it is exposed to light or when light is removed from the same. There are other methods by which the variation of energy during the "induction" and "deduction" periods may be determined. The author is now engaged in the elucidation of the laws concerning the induction and deduction periods of energy which up to the present have only the character of qualitative observations.*

The Influence of Small Traces of Air and Water upon the Mixture of Pure Chlorine and Carbon Monoxide (and other Gaseous Systems).

The admixture of small traces of air with the reacting gases produces a most remarkable retarding effect upon the velocity of the reaction. BUNSEN and ROSCOE found that this held for a mixture of chlorine and hydrogen, so that it appears to be a general rule for all gaseous systems.

Two "quartz vessels" were placed one behind the other, both vessels were evacuated and treated in exactly the same way, and finally filled with carbon monoxide from the same sample at the same time. Chlorine from the same sample was driven by means of the same concentrated sulphuric acid (which, for reasons mentioned before, it was impossible to keep for any length of time quite free from

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* As to the chemical induction and deduction periods it is evident that, since velocity of reaction follows the law of action of mass, when the molecules taking part in the reaction have attained, under the influence of light, a constant value of their chemical potentials, the same law of mass action must also be the governing principle for the velocity of reaction at any given moment of the chemical induction and deduction periods, only the velocity constant, K in equation (3), will vary in time as the chemical potentials of the reacting substances change.

air) first into the vessel behind, and then, about a quarter of an hour later, into the vessel in front. Both vessels were simultaneously exposed in the bath to the same acetylene light, but the velocity of combination of chlorine and carbon monoxide was considerably slower in the front vessel than in the vessel placed behind it. (The opposite would have been expected.) (See Curves 1 and 2 of Tables III. and IV.)

The accelerating influence of water vapour upon the velocity of reaction is very great. The same glass bulb was filled with the chlorine and carbon monoxide, both freshly prepared in the dark. The chlorine was in both cases absolutely the same, *i.e.*, equally dry; the freshly prepared carbon monoxide on the contrary was allowed to bubble in the two experiments through different heights of sulphuric acid in the bulb S (fig. 1, p. 340) by tilting the bulb more in the second experiment than in the first. The sulphuric acid was the same in both cases, and each time was first heated in the bulb in a vacuum till it was perfectly freed from any gas. The freshly-prepared carbon monoxide was thus most probably in one case a little drier than in the other, and the difference in the quantity of water still retained by the carbon monoxide evidently could only be exceedingly very small. The difference in the speed of combination of carbon monoxide and chlorine on the contrary proved to be very great. (See curves of Table V.)

A further experiment was thus made:—The gases were brought into the glass bulb containing ordinary concentrated sulphuric acid freed from air, well shaken, then left in the dark for about two days, and then exposed to the powerful acetylene light; no reaction could be observed after several hours during two days, but on exposure to sunlight the two gases combined, though only exceedingly slowly. Since the concentrated sulphuric acid was of sp. gr. 1·84, it contained water, and it must still have had (REGNAULT) a vapour pressure of water, though an extraordinarily small one, so that the pressure of water vapour was still not absolutely excluded, and this may be the cause why an exceedingly slow reaction could still take place in sunlight.

Thus, the less water vapour is present with the gases the slower is the reaction. Reaction takes place in the presence of an exceedingly small quantity of water vapour in the mixture; small, apparently immeasureable, differences in the amount of water vapour, at any rate when the vapour is present only in small quantities, produces great differences in the velocity of the reaction.

It should be observed that we could not use greater quantities of water vapour for the experiments, still less could we have the gases in presence of water, because water decomposes the carbonyl chloride formed, giving carbonic and hydrochloric acids.

BUNSEN and ROSCOE used their mixture of chlorine and hydrogen in the presence of water saturated with these gases. PRINGSHEIM found later on that, if chlorine and hydrogen are taken quite dry, they do not combine in light at all. This phenomenon PRINGSHEIM thought possible to explain in the following manner:—The chlorine and hydrogen, according to his conception, do not combine directly to hydrochloric acid, but chlorine and water first form an intermediate compound hypochlorous acid (and hydrogen), which with hydrogen forms the hydrochloric acid, setting free the same molecules of water which are again used in the reaction, *i.e.*, instead of having $H_2 + Cl_2 = 2HCL$, we have $Cl_2 + H_2O = Cl_2O + H_2$; $Cl_2O + H_4 = 2HCl + H_2O$. I doubt the correctness of this explanation for the following reason:—It is known that chlorine and water, when exposed to light, form not hypochlorous acid but hydrochloric acid (WITTWER, BUNSEN, and ROSCOE).* Still the difficulty remains that chlorine and hydrogen are not the only system having such properties. The system chlorine and carbon monoxide exhibits the same property. We also know that ammonia and hydrochloric acid do not combine when perfectly dry; carbon monoxide and hydrogen do not explode when perfectly dry (DIXON); perfectly dry hydrogen peroxide does not act upon a photographic plate (RUSSELL). For this reason it seems that in gaseous systems a phenomenon is met which in other cases is called "catalytic action," in which a reaction is accelerated or caused by the presence of an extraneous substance, which apparently or in reality takes no part in the reaction, *e.g.*, the action of platinum-black upon the decomposition of hydrogen peroxide, &c.

The catalytic action of gases upon the velocity of reaction in the gaseous systems may be divided into "catalytic action with an accelerating influence" (to this belongs the action of water vapour upon the gaseous systems mentioned above) and into "catalytic action with a retarding influence" (to this belongs the action of oxygen or air upon the systems chlorine and hydrogen or chlorine and carbon monoxide). This division is, however, of a purely formal nature, and hardly anything is known of the ultimate nature of the phenomenon.

Velocity of Chemical Reaction and Chemical Equilibrium in Light.

Having thus established beyond any doubt that the velocity of reaction in light is governed in homogeneous systems by the same law of mass action as in the dark, the influence of temperature as well as of the intensity of light upon the value of the velocity constant, as well as the connexion between the velocity constant and the wave length on the monochromatic light, have still to be investigated; and finally the investigation of heterogeneous systems regulated by other fundamental principles remains necessary. This will form the subject of the author's future investigation.

On the other hand the solution of the problem for chemical kinetics in light evidently already shows with perfect certainty that the law of mass action, which governs chemical equilibrium in homogeneous systems in the dark must necessarily also govern chemical equilibrium in the light. It is most remarkable that we do not

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* Professor DIXON, in a private communication, makes a better suggestion—that the reaction between hydrogen and chlorine is to be conceived thus:—$Cl_2 + H_2O = 2HCl + \widehat{O}$ (nascent); $\widehat{O} + H_2 = H_2O$, the first equation being reversible.

know of any reversible system, in which the two opposite reactions do not go on in the dark but go on in the light. But we do know systems in which one reaction goes on in the dark and is modified in light, while the opposite reaction goes on in the light only, *e.g.*,

$$\begin{array}{lcl} 2\text{AgCl in solution} & \rightleftarrows & \text{Ag}_2 \text{ (or Ag}_2\text{Cl) in sol.} + \text{Cl}_2 \text{ in sol.} \\ \quad\downarrow\uparrow & & \qquad\downarrow\uparrow \\ \text{AgCl solid} & & \text{Ag (or Ag}_2\text{Cl) solid.} \end{array}$$

Here is an homogeneous system, on the one hand silver chloride is decomposed by light into silver and chlorine or silver sub-chloride and chlorine (this question is at present unsettled), on the other hand silver (or silver sub-chloride) and chlorine combine in the dark forming silver chloride, and this combination evidently goes on in light also (though probably with a different speed). Let the volume of the solution be V. For the first reaction in light we have according to the law found above $\frac{dx}{d\tau} = c\,\frac{(\text{A} - x)^2}{v^2}$, where $\frac{\text{A} - x}{v}$ is the concentration of the molecules of silver chloride in solution (however small this may be) at the time τ, and x/v is the concentration of the chlorine as well as of the silver molecules formed in solution; c is the velocity constant which changes with the intensity and composition of the light passing through the system. For the second reaction we have according to the law of mass action in the dark $\left(\frac{dx}{d\tau}\right)' = c'\left(\frac{x}{v}\right)^2$, where c' is the velocity constant for the reaction in which silver chloride is formed from silver and chlorine. The velocity constant in light is different from that in the dark, say c'', however small this difference may be, for the reason that chlorine and silver are in a different state of energy in the dark and in the light. It follows from this that when equilibrium takes place in the light, or when no further variation in the masses takes place,

$$\frac{dx}{d\tau} - \left(\frac{dx}{d\tau}\right)' = 0\,; \qquad \frac{c\,(\text{A} - x)^2}{v^2} - c''\left(\frac{x}{v}\right)^2 = 0\,; \qquad \frac{(\text{A} - x)^2}{x^2} = \frac{c''}{c} = \text{K}\,;$$

that is, we must at the point of equilibrium get a constant K, which will regulate the masses forming the reversible system with the variation of the volume or of the concentrations or of the partial pressures of the substances, because both opposite reactions have each a separate velocity constant before equilibrium. Though this proof of the necessity of the existence of a constant of equilibrium is absolute, it would have been very valuable and desirable to directly illustrate the equilibrium constant K in a reversible system from the varying masses at equilibrium, as we succeeded in doing for the velocity of reaction. Unfortunately there is not one homogeneous system known where such a proof could be successfully carried out. It is well to remember the enormous difficulties one meets with in this region, when even such apparently simple reactions as the combination of carbon monoxide and chlorine or of chlorine and hydrogen, are to be measured quantitatively. The author is at present engaged in such attempts to test directly the constants of equilibrium, not so much because the law needs further confirmation, as on account of the very interesting thermodynamic connection which must exist between the constant of equilibrium, the heat of reaction in light, and the absolute temperature on the one hand, and the constant of equilibrium and the intensity of light on the other.

APPENDIX : *Thermodynamical Considerations.*

The above experimental results find their rational basis and explanation in thermodynamics. The condition of equilibrium in a homogeneous system, when only chemical, thermal, and mechanical energy are taken into consideration, is according to GIBBS: $dE = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n \geqq 0$, where E is the energy, η the entropy, $m_1, m_2 \ldots m_n$ the quantities of the substances $S_1, S_2 \ldots, \mu_1, \mu_2$ the chemical potentials of $S_1, S_2 \ldots$ Let us now assume that the system is exposed to light of constant intensity and composition, and that the system is in such thin layer that the intensity of the light is the same in all parts of it. Since all substances absorb light and the light absorbed is not completely transformed into heat, a part of the light will appear as other forms of kinetic energy of the atoms and molecules. From a molecular mechanical point of view this will mean that under the influence of light the amount of work present in the molecules as energy of the atoms increases. Obviously the ratio of the amount of light transformed into heat to that transformed into kinetic energy of the atoms is not constant. At first the energy of the atoms and molecules gradually increases (induction period of energy), until a reaction, a shifting of the point of equilibrium to another one, becomes possible (chemical induction period), which is observed by an increase of the velocity constant. Under the action of light the storage of energy in the atoms and molecules ultimately reaches a maximum, after which light produces no more strain upon the atoms, preventing them only from losing the energy once acquired, and the whole of the light entering into the system is transformed into heat. This maximum kinetic energy of the atoms is a function of the intensity and composition of light, of the nature of the substance, of the surrounding medium, &c., and becomes apparent in the fact that a velocity constant, indicative of constant properties of the atoms and molecules, is obtained. When light is removed from the system the energy stored in the atoms and molecules, under the impulses of the light waves, gradually disappears, changing either into chemical energy and heat (as long as the reaction continues in the dark, chemical deduction period) or into heat alone (deduction period of energy). When the maximum kinetic energy of the atoms is reached under the action of light, it is evident that the energy stored up must be directly proportional to the mass of each substance. To the above equation for equilibrium the terms $\nu_1 dm_1 + \nu_2 dm_2 \ldots + \nu_n dm_n$ must therefore be added. By means of a cycle process at a constant temperature it can also be shown that the entropy of the system changes in light. When chemical transformation takes place in the system this is also accompanied by variation in its mechanical energy. The kinetic explanation of the phenomena of absorption, dispersion, fluorescence, by STOKES and HELMHOLTZ, led the author to the conclusion that the energy stored in the atoms and molecules under the action of light, partly transforms into chemical, partly into kinetic energy *sui generis*, which may be called light-kinetic energy,—a conclusion strengthened by the author's experiments on the effect of light upon two plates of the same element, when they are immersed in a liquid, connected with a galvanometer, and one plate is exposed to light while the other is kept in the dark. Thus, under the action of light, the chemical potential of each substance increases and each substance acquires a new light-kinetic potential. Instead of equation (i.) we now have for equilibrium in light

$$dE + dE_1 = dE' = t'd\eta' - p'dv' + \mu_1'dm_1' + \mu_2'dm_2' \ldots + \mu_n dm_n'$$
$$+ \lambda_1'dm_1' + \lambda_2'dm_2' \ldots + \lambda_n'dm_n' \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{ii.}).$$

Integrating this equation, then differentiating in the most general way and subtracting (ii.) we get

$$\eta'dt' - v'dp' + m'd\lambda_1' + m'd\mu_1' \ldots + m_n'd\lambda_n' + m_n'd\mu_n' = 0 \quad . \quad . \quad (\text{iii.}).$$

General considerations show that for the system to be in equilibrium the sum of both potentials of each substance must be constant through the whole system, *i.e.*, $\mu_1' + \lambda_1' = c_1$, $\mu_2' + \lambda_2' = c_2 \ldots (\gamma)$. (iii.) and ($\gamma$) give the variation of temperature or pressure, or of the chemical potential, or of the light-kinetic potential, or of several of them, with the variation of one or more of the rest of the variables. The sum of both potentials $\mu_1' + \lambda_1'$ being $= \left(\frac{dE + dE_1}{dm_1}\right)_{\eta_1' v_1' m_2' \ldots m_n'}$, and the equation for chemical reaction being $n_1 A_1 + n_2 A_2 = n_3 A_3$ (α), we still find that, under due considerations,

$$n_1(\mu_1' + \lambda_1') + n_2(\mu_2' + \lambda_2') = n_3(\mu_3' + \lambda_3') \quad . \quad . \quad . \quad . \quad . \quad (\beta).$$

Taking in equation (iii.) the grammolecule as unit of mass (which is not the case in GIBBS' deductions), in order to get subsequently a result which in its form and content expresses our present molecular conceptions of a chemical reaction, &c., we get, if the system is a gaseous one, consisting of one substance only, and its total mass is m_1' grammolecules, that the total chemical energy is $\mu_1'm_1'$, the variation in the same $m_1'd\mu_1'$, the total light-kinetic energy is $\lambda_1'm_1'$, the variation in the same $m_1'd\lambda_1'$, the total mechanical energy $p'v' = m_1'RT$, since $p'v'$ of 1 grammolecule $=$ RT, and $v'\,dp' = v'd\left(\frac{m_1'RT}{v'}\right)$, the total entropy of the mass $\eta' = m_1'\left(\frac{H'}{T} + K'\right)$, when the entropy of 1 grammolecule $= \frac{H' \text{ (of 1 grammolecule)}}{T} + K'$. Thus putting in (iii.) these values and integrating we get $\mu_1 + \lambda_1 = RT + RT \log \frac{m_1'}{v'} - H' \log T + K'T + K''$, where

K′ and K″ are integration constants. Assuming now that the system consists of several substances, as given in (α), and that the law of DALTON holds good for the chemical and for the light-kinetic potentials, then we get from (β) that

$$\log\left\{\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2}\Big/\left(\frac{m_3'}{v'}\right)^{n_3}\right\} = \frac{1}{RT}[(n_3K_3' - n_1K_1' - n_2K_2')T - (n_2 + n_1 - n_3)RT$$
$$+ (n_1H_1' + n_2H_2' - n_3H_3')\log T + (n_3K_3'' - n_1K_1'' - n_2K_2'')] \quad . \quad . \quad \text{(iv.)},$$

where $\frac{m_1'}{v'}$, $\frac{m_2'}{v'}$, $\frac{m_3}{v'}$ are the concentrations of each substance expressed in grammolecules, n_1, n_2 . . . the numbers of grammolecules of each substance taking part in the reaction, $n_3K_3' - n_1K_1' - n_2K_2' =$ constant $K^{\text{iv.}}$, $-(n_2+n_1-n_3)$ RT is the work done by the system (α) during the transformation in light, $(n_1H_1' + n_2H_2' - n_3H_3')\log T + (n_3K_3'' - n_1K_1'' - n_2K_2'')$ is the heat of reaction *in light.* Thus the connection between the logarithm of the constant of chemical equilibrium in homogeneous systems in light, the heat of reaction or of transformation of n_1 grammolecules of S_1 *plus* n_2 grammolecules of S_2 into n_3 grammolecules of S_3 in light, the work done during the transformation, and the absolute temperature, follows the same law in light as it does in the dark. The effect of light upon a system therefore consists in shifting it to a new point of equilibrium. It is further easy to show that at a constant volume, since the work $-(n_2 + n_1 - n_3)RT = 0$, and $\eta't'$ can be put $= C_sT$, where C_s is the specific heat at a constant volume, T the absolute temperature, an equation is arrived at, which after differentiation gives $\frac{d}{dT}\left[\log\left(\frac{m_1'}{v'}\right)^{n_1} + \log\left(\frac{m_2'}{v'}\right)^{n_2} - \log\left(\frac{m_3'}{v'}\right)^{n_3}\right] = \frac{A + BT}{RT^2}$ (v.), where A and B are constants (equation of VAN'T HOFF and KOOY), which at a constant temperature gives $\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2}\Big/\left(\frac{m_3'}{v'}\right)^{n_3} =$ constant (vi.), *i.e.*, the law of mass action holds good for chemical equilibrium in light, as found experimentally. Decomposing this equation for homogeneous systems in the usual manner into two, giving the two opposite velocities of reaction, which at equilibrium become equal, we get

$$\left(\frac{dx}{dT}\right)' = c'\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2} \text{ and } \left(\frac{dx}{dT}\right)'' = c''\left(\frac{m_3'}{v'}\right)^{n_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)},$$

i.e., the velocity of chemical reaction in light must also follow the laws of mass action, as found experimentally.

In conclusion, I should like to express my thanks to the Managers of the Davy-Faraday Laboratory of the Royal Institution for having allowed me to make use of the splendid arrangements of the Laboratory, and especially to Dr. LUDWIG MOND, who by his kind assistance has enabled me to undertake and carry out the above research, and who by his valuable advice on many occasions has very essentially contributed to the success of the same.