STUDIES
ON
THE PHOTOCHEMISTRY OF CHLORINE.

by

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CONTENTS.

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Introductory Note.

Although certain trends in the course of the photo-reaction between hydrogen and chlorine have been established with moderate certainty, it cannot be claimed that the complete mechanism and kinetics are entirely elucidated.

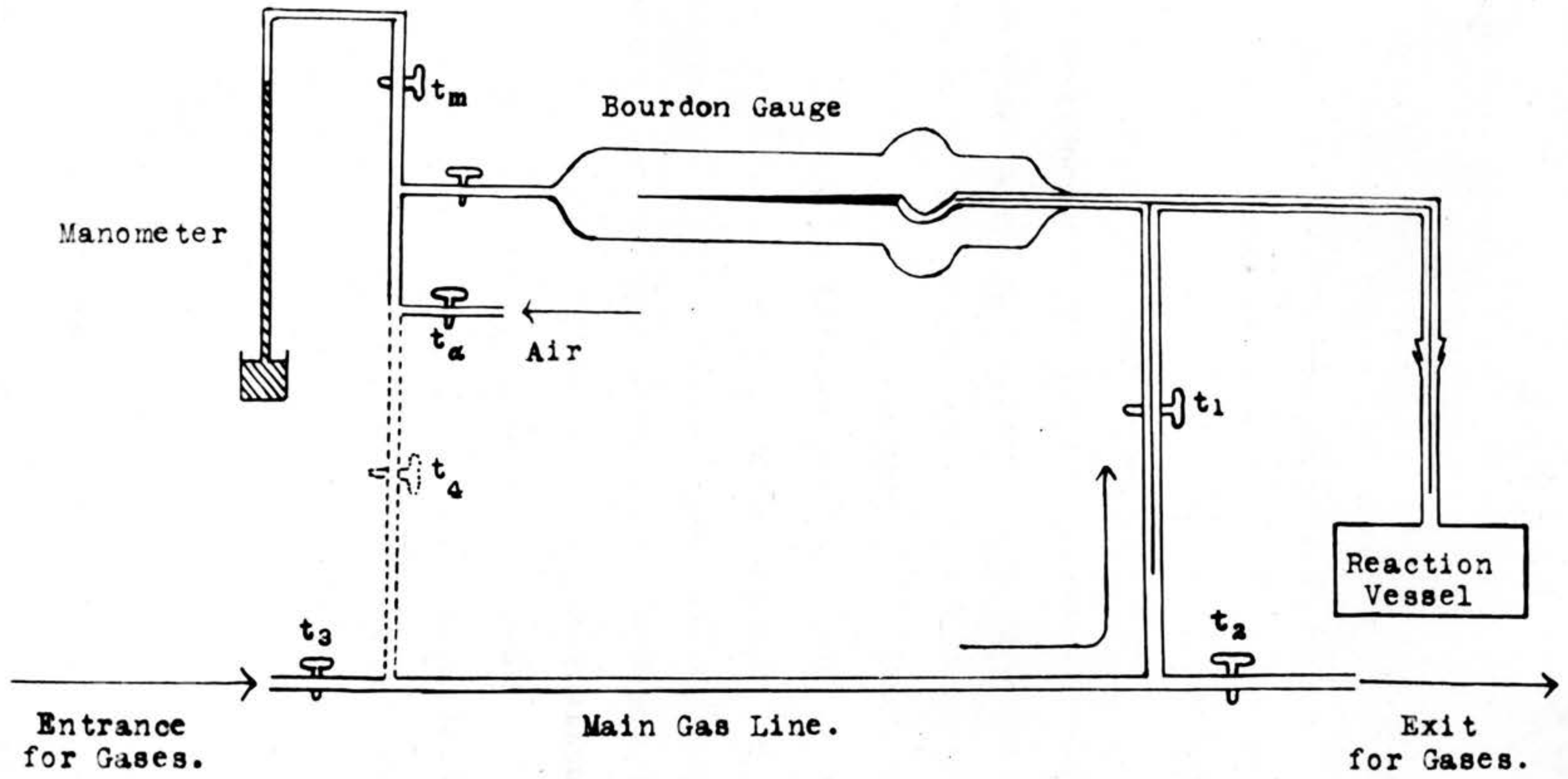
One controversial point concerns the production of various particles, which act as intermediates in the reaction. In particular, it has been suggested by various investigators that a molecule, composed of three atoms of chlorine, might be formed under certain circumstances.

The presence of this particle was also suspected in certain Budde effect measurements. These have been more intensively investigated, as described in Part I.

Other photo-reactions, in which it was anticipated that the particle might be present as an intermediate, have also been examined.

In Part II are described some of the kinetics of the reaction between toluene and chlorine, in which both a photo- and thermal reaction of considerable magnitude are present.

Part III concerns the photo-reaction between methane and chlorine, which has here been investigated as analogous to the corresponding hydrogen-chlorine reaction.



Bourdon Gauge
Manometer
t_m
t_a
Air
t_4
t_1
Reaction Vessel
t_3
t_2
Entrance for Gases.
Main Gas Line.
Exit for Gases.

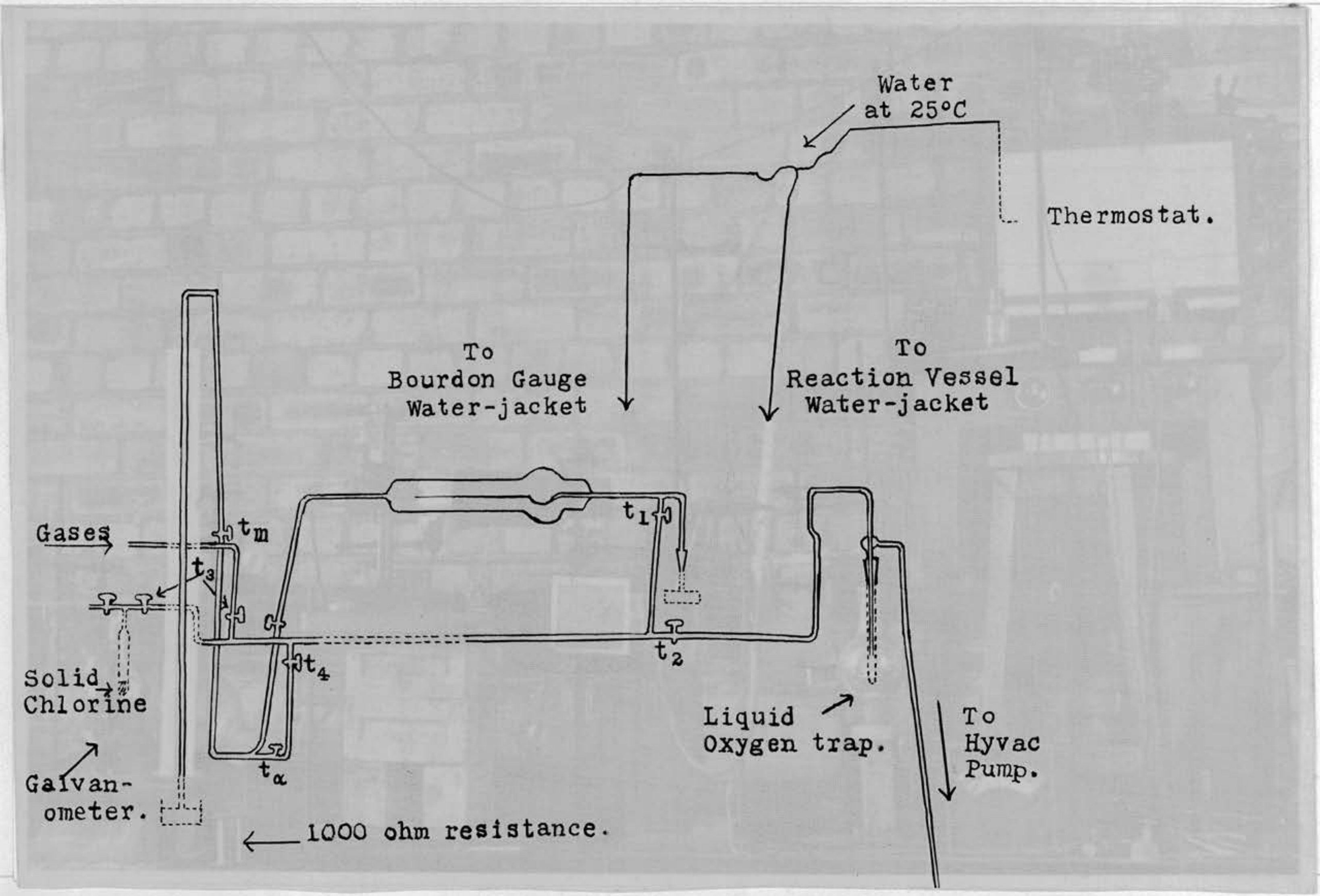
EXPERIMENTAL.

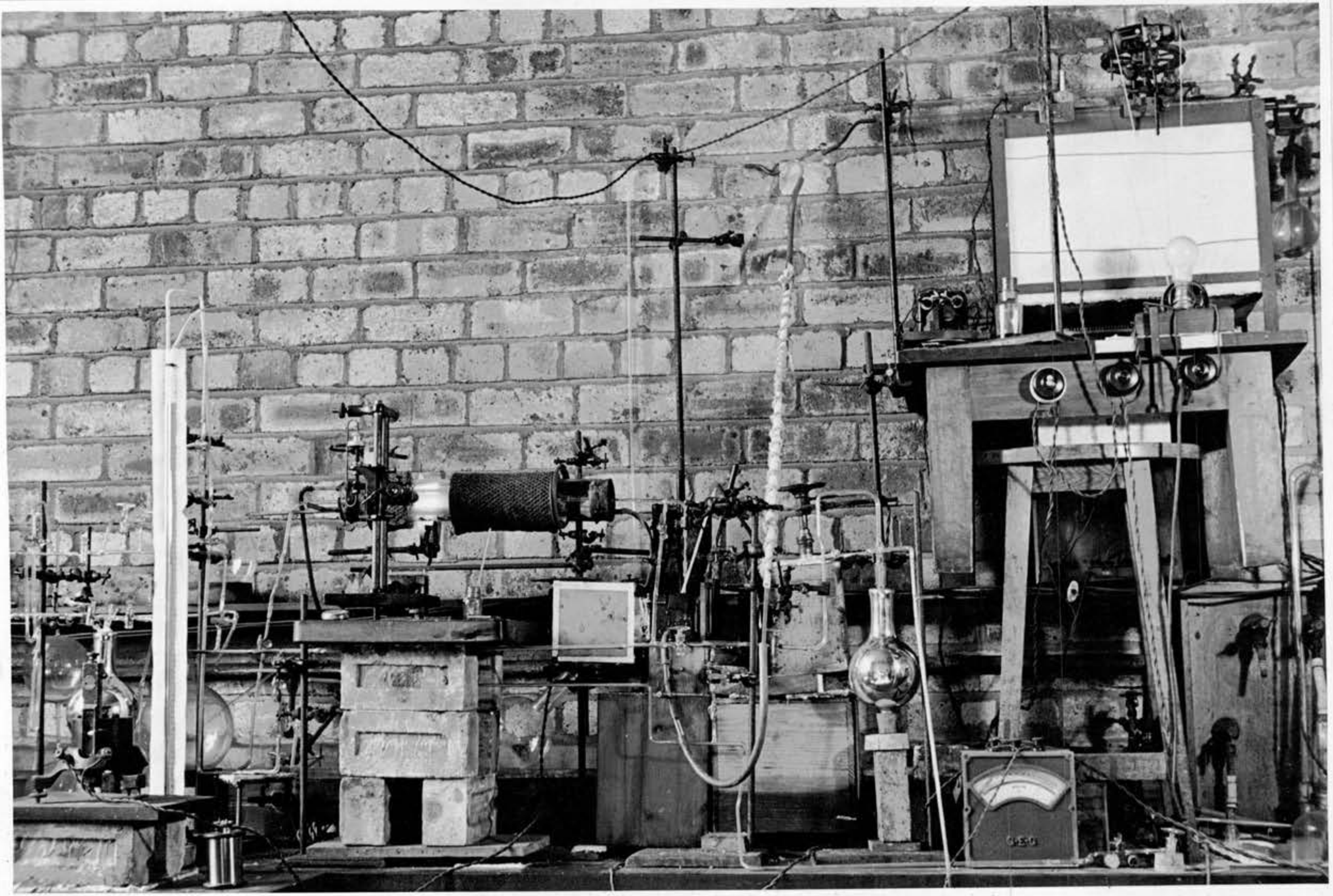
Apparatus:

The essential features of the apparatus, as used in the subsequent investigations, can be seen in the diagram opposite.

The pressure of gas present in the reaction vessel was "balanced" with a corresponding pressure of dry air, in order that the Bourdon gauge pointer should remain at its null position, the actual amount of air added being indicated on the manometer. Small pressure changes in the gas system were recorded directly on the Bourdon gauge by means of a telescope focussed on the gauge pointer. The Bourdon gauge itself was kept at constant temperature by enclosure in a cylindrical glass water-jacket.

Reaction vessels of various sizes and composition were used throughout the investigations, and either sealed directly on to the apparatus, or attached by a glass joint, as indicated in diagram. The vessels were also thermostatted, using a metal box arrangement with windows placed to allow light of a suitable wavelength to pass through when certain shutters were opened, but preventing the entry of stray light to the reaction vessel.


Water at 25°C
Thermostat.
To Bourdon Gauge Water-jacket
To Reaction Vessel Water-jacket
Gases
t_m
t_3
t_1
t_2
t_4
t_α
Solid Chlorine
Galvan-ometer.
1000 ohm resistance.
Liquid Oxygen trap.
To Hyvac Pump.



The apparatus could, at any stage, be evacuated by using a Cenco Hyvac pump, capable of giving a vacuum of 0.001 mm of mercury. The gases, before reaching the pump, were passed through a liquid oxygen trap to remove those easily condensable gases, which would attack or dissolve in the oil of the pump. Before starting a series of observations, evacuation was normally carried out for at least 30 minutes.

All glass joints and taps were lubricated using a vacuum grease, Apiezon L, composed of hydrocarbons of high boiling point, which had previously been found[1] to possess a good resistance to the action of chlorine, yielding products which gave the minimum interference as inhibitors in photo-reactions. In the chlorine-toluene reaction, a certain amount of difficulty was experienced, due to the solubility of the toluene in the Apiezon L grease. A starch-glycerol lubricant was substituted, but it possessed the disadvantage of stiffening after about four days use, when renewal became necessary.

The thermostat itself, shown in the photograph, was fed with a steady stream of water, by means of a constant level device. The heating arrangement consisted in 2 long carbon filament lamps immersed in the water, and, if necessary, this was augmented by three electrical heaters placed under the thermostat tank. The heating action was controlled by a toluene regulator, capable of maintaining the temperature of the water within limits of ± 0.02°C. The water flowed by gravity to the Bourdon gauge, and reaction vessel water-jackets, thereby producing a constant temperature of usually 25°C, and was then rejected at the sink.

A 125 watt pearl Osira mercury lamp was used as the source of illumination. It was run at 230 volts and kept at this value, within a limit of ± 1%, by means of a Solus stabiliser. This gave a sufficiently steady intensity of light.

The lamp was enclosed in a ventilated box arrangement, with an aperture, about one inch in diameter. The light beam then passed through a filter containing a 5% solution of copper sulphate, to remove heat rays. This was contained either in a plane-sided glass cell, 2 cm in depth, or, if concentration of the beam was also desired, in a spherical flask, about 500 ml. in volume.

The light was then filtered to secure the desired wavelength. In the case of a wavelength of 365 mu, a Chance glass filter, number 18a, was used. For a wavelength of 406 mu, a two-compartment plane-sided rectangular glass cell was inserted, one compartment of which contained a solution of $Cu(NO_3)_2.6H_2O$ (200 g. dissolved in 100 ml. water) of 2 cm depth, and the other compartment, a solution of iodine in carbon tetrachloride (0.75 g. dissolved in 100 ml. CCl_4) of 1 cm. depth, as described by Bowen.[2]

When it became necessary to reduce the light intensity, the beam was passed through a variable number of coloured glass sheets, capable of being readily inserted and removed.

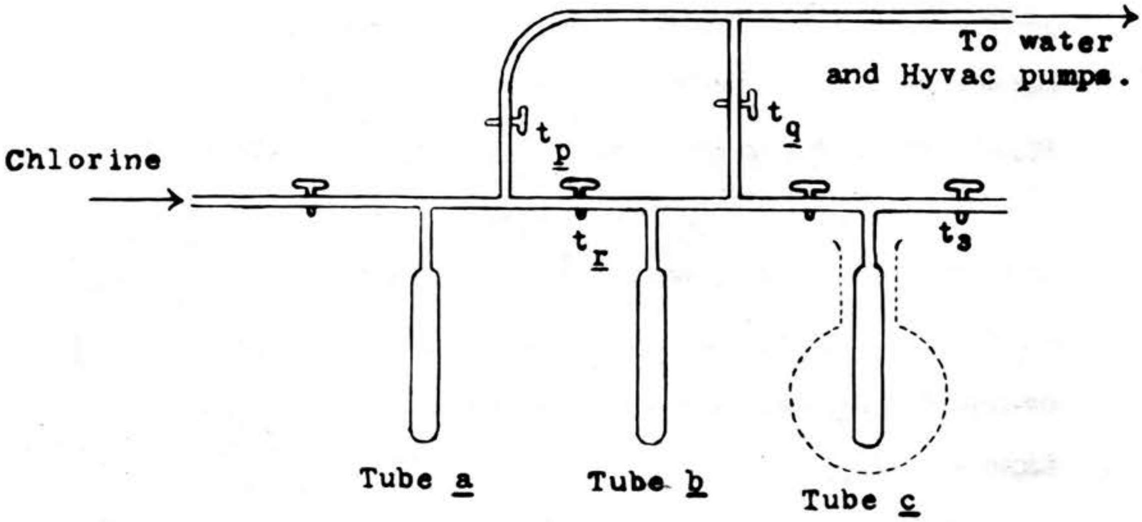
At this stage, a simple shutter arrangement was included, allowing the light to be completely and instantaneously cut off.

The beam, usually narrowed by an aperture, was then passed through the one window of the reaction vessel water-jacket, through the thermostat liquid, and finally into the reaction vessel itself. Great care was taken, in all instances, to ensure that the light beam should pass, to as great an extent as possible, through the entire reaction vessel, but that no light should by-pass it completely. Immediately behind the reaction vessel, another shutter arrangement was inserted, to allow, if necessary, illumination of the reaction vessel, without the light penetrating further.

After the light beam had passed through the rear-window of the water-jacket, it fell immediately on to the face of an "Eel" photronic cell, contained in a wooden box, and completely impermeable to other light. This box was sealed to the reaction vessel water-jacket in such a way that again no extraneous light was allowed to enter.

The photo-cell was connected to a sensitive mirror galvanometer, situated nearby, and covered in by an iron box, to protect it from stray magnetic effects. In the preliminary experiments on the chlorine-toluene reaction, a variable resistance was also connected in parallel with the galvanometer, to act as a shunt and secure a suitable deflection of the mirror. This did not prove entirely satisfactory, however, and in later observations, instead of the variable resistance, a fixed 1000 ohm resistance was substituted.

Final Purification of Chlorine - diagrammatic.



Purification of the Reactants.

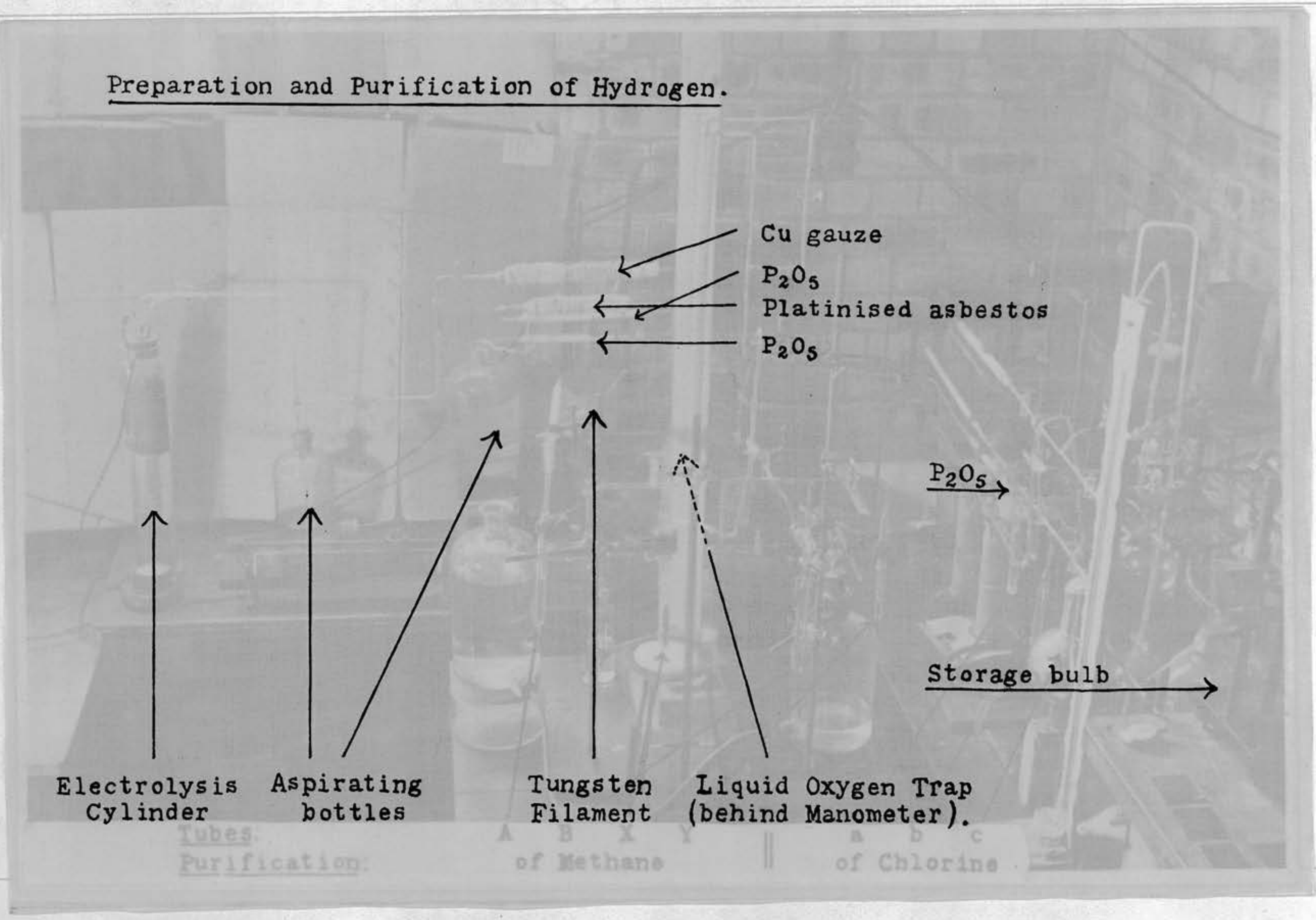
1. Chlorine:

It has been previously found that cylinder chlorine can be sufficiently purified to yield satisfactory results in photo-chemical experiments, and this source was used.

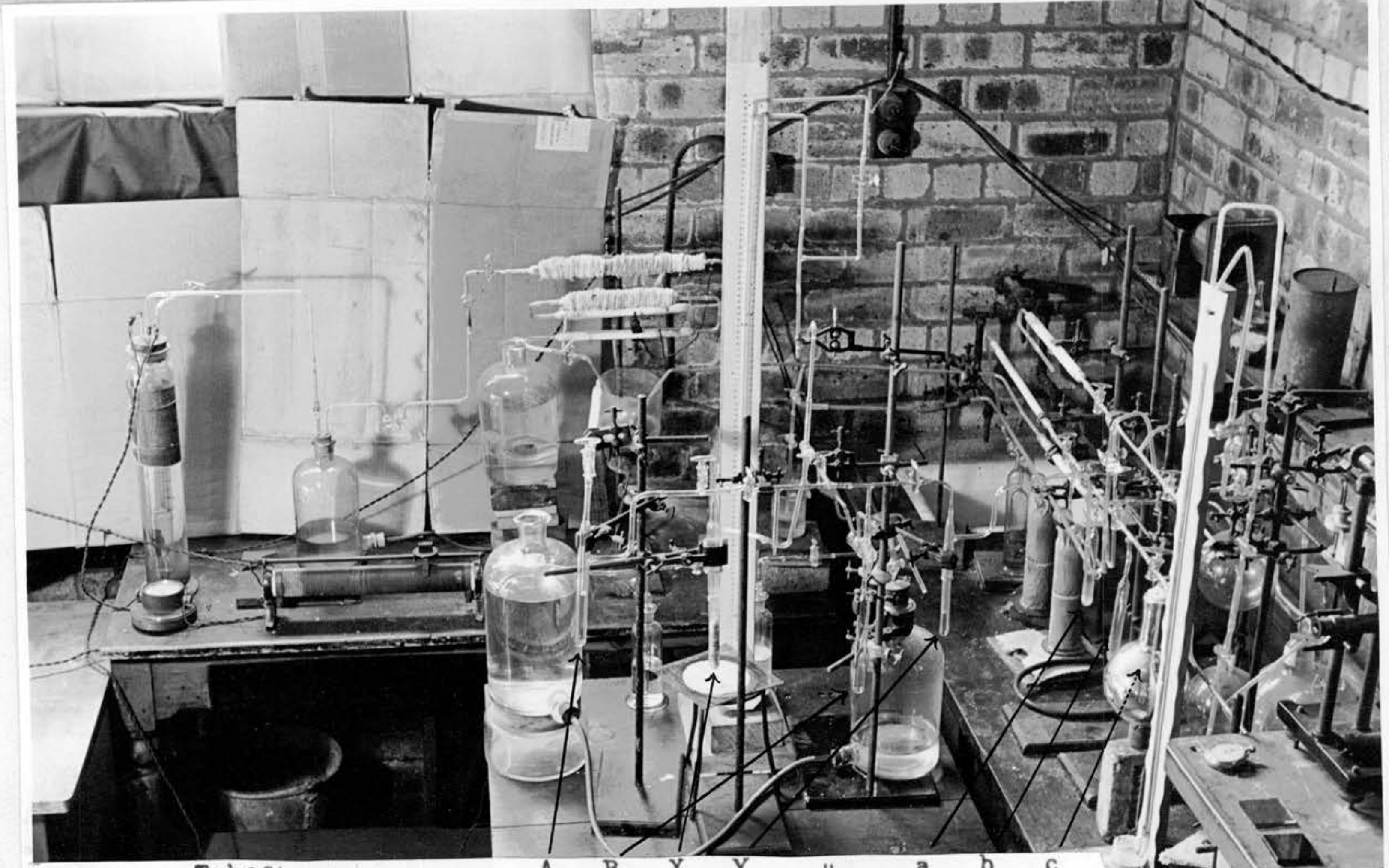
The chlorine was first passed through two washbottles containing alkaline 2 N potassium permanganate solution, followed by one containing concentrated sulphuric acid. Final drying was achieved by passage over phosphorus pentoxide.

The dry chlorine was then slowly collected in the two tubes a and b by cooling them externally with liquid oxygen. Gaseous impurities were occasionally drawn off by the oil pump, through taps p and q.

After about 10 ml. of solid chlorine had been collected in each tube, it was entirely transferred to tube a, and, after evacuation for a few minutes using the oil pump, fractional distillation was carried out between the tubes a and b. The liquid oxygen was removed from around tube a, the chlorine allowed to liquify, and one-tenth drawn off through the tap p using the water pump. Tap p was closed, tap r opened, and tube b washed out several times with chlorine gas. Finally, distillation was



Preparation and Purification of Hydrogen.



<u>Tubes</u>: A B X Y || a b c

<u>Purification</u>: of Methane || of Chlorine

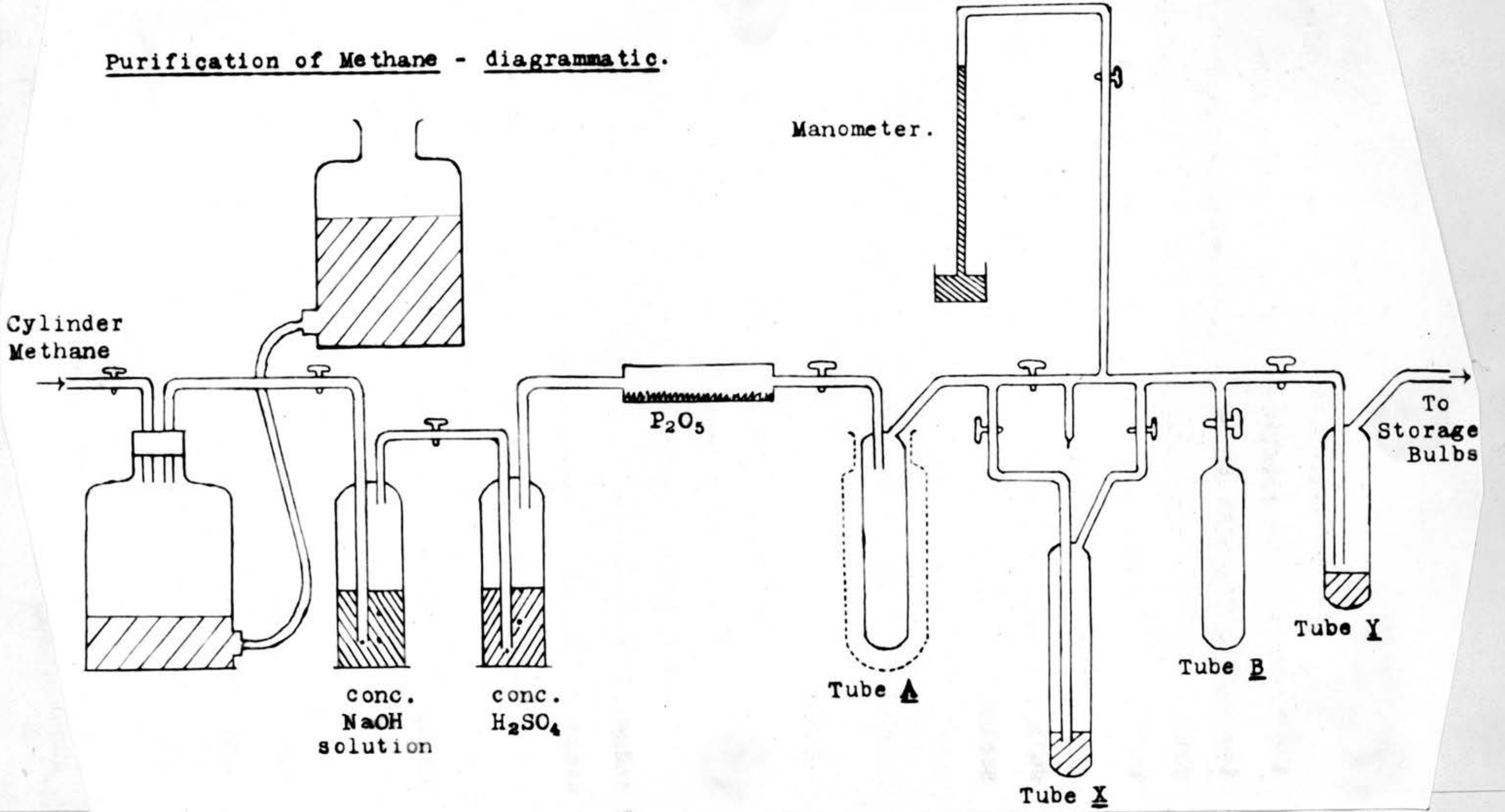
carried out by surrounding tube b with liquid oxygen. Nine-tenths of the remaining chlorine was distilled over, the remaining tenth being rejected through tap p. Occasionally, during the distillation, the chlorine in both tubes was solidified, and any extraneous gases remaining were removed by evacuation using the oil pump. In a similar way, the chlorine was distilled back to tube a.

These distillations were normally carried out four times, and the chlorine finally isolated and kept solid in tube c by surrounding with a flask of liquid oxygen.

2. Hydrogen:

This was prepared by electrolysing a 10% caustic soda solution containing a little baryta, the platinum cathode being isolated by a cylindrical glass tube. The hydrogen was passed, using glass tubing throughout, to two aspirating bottles, arranged so that the collection of the gas would take place under a slight pressure of water, thus ensuring no possible direct leakage of air into the apparatus. This was carried out immediately before the purification of the hydrogen, since on standing, air, dissolved in the water, might enter the gas.

Purification of Methane - diagrammatic.



The purification consisted in slowly passing the hydrogen over electrically-heated copper gauze (to remove the bulk of the oxygen) over phosphorus pentoxide, over platinised asbestos, also electrically heated, and again over phosphorous pentoxide. This was followed by passage over a tungsten filament at dull red heat, the bulb containing the filament being cooled by a water jacket; and finally passing the gas through a liquid oxygen trap and again over phosphorus pentoxide. It was collected in large bulbs.

3. Methane:

Cylinder methane (containing 97.52% CH_4, 2.42% N_2, 0.06% CO, no measurable quantity of ethane, unsaturated hydrocarbons, O_2, CO_2, H_2)* was collected under slight pressure in the aspirator, as shown in diagram, and slowly bubbled through two washbottles containing first, strong caustic soda solution, to remove traces of any acidic impurities, and then through concentrated sulphuric acid to remove traces of basic impurities, at the same time drying the gas to some extent. Final drying was accomplished by passage over 12 inches of phosphorus pentoxide in a narrow glass tube, and the methane liquified in tube A by surrounding with a flask of liquid air.

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* I am indebted to Dr Prot for the use of the figures quoted above.

As traces of the "permanent" gases, oxygen and nitrogen in particular, gradually accumulate at this stage, the gases above the liquid methane were occasionally pulled off by means of the oil pump. In this way, about 20 ml. of relatively pure liquid methane were collected.

The final purification consisted in distilling the liquid methane twice between tubes A and B, removing the first and last tenth each time. It was then distilled through molten sodium in tube X, collected again in tube B, and finally returned directly as before to tube A.

The methane was then slowly passed through the molten sodium in tube X, over molten sodium in tube Y, and immediately transferred to 2 large glass reservoirs, in which it was stored. The whole apparatus, from the aspirator to the storage bulbs, was constructed of soda-glass, thus ensuring, as far as possible, no leakage of gases.

4. Toluene:

B.D.H. sulphur-free toluene, dried over solid calcium chloride, was transferred after a preliminary fractionation, to a glass bulb on the inert gas line, attached by a vacuum joint. It was again distilled, with liquid oxygen. rejecting the first and last fifth, into another glass bulb, fitted with a large, well-greased, tap. The toluene was finally solidified by surrounding the tube with liquid oxygen, and the space above evacuated for fifteen minutes using the oil pump.

5. Oxygen:

Cylinder oxygen was purified by slowing passing it through a wash-bottle containing potassium permanganate solution, then through concentrated sulphuric acid, over phosphorus pentoxide and through a liquid oxygen trap. The gas was finally stored in a 2-litre glass bulb.

6. Nitrogen:

Cylinder nitrogen was purified by slow passage over heated copper gauze, then over phosphorus pentoxide and molten sodium and finally through a liquid oxygen trap. It was collected in glass bulbs.

DETAILED EXPERIMENTAL PROCEDURE TO INTRODUCE EXACTLY 300 mm PRESSURE OF A GAS INTO THE REACTION VESSEL.

The apparatus was evacuated for at least 30 minutes with taps 1, 2, 4, and m, open and taps 3 and α closed, assuming that the purified gas is present beyond tap 3.

To minimise the presence of mercury vapour in the reaction vessel, tap m was then closed and evacuation continued for another quarter of an hour. Taps 1 and 4 were closed simultaneously, and the absence of any slight leaks in the system confirmed by the Bourdon gauge pointer remaining steady.

At this stage, tap m was again opened, thus directly connecting the manometer with the Bourdon gauge.

The required gas was now introduced to the main gas line by closing tap 2, and opening and closing tap 3.

It was customary to "wash out" the reaction vessel with the gas, before its final introduction. This was done by gradually opening tap 1, allowing a few mm of gas to enter - as measured on the Bourdon gauge - then evacuating both the main line by opening tap 2, and finally the reaction vessel itself by opening tap 1. This was carried out several times to secure the complete absence of gaseous impurities in the reaction vessel. The pointer of the gauge should finally return to its original position when evacuation of the vessel is complete. The main line was again filled with gas.

The final entry of 300 mm of the gas into the reaction vessel was carried out by gradually opening taps 1 and α simultaneously, and varying the rates of entry of gas and air so that the Bourdon gauge pointer remained almost stationary at its null position. The mercury in the experimented manometer gradually dropped and when almost the correct amount of gas had been added to the reaction vessel, (as measured by comparison with the adjacent standard manometer) tap 1 was closed. Air continued slowly to enter through tap α , until the mercury in the experimental manometer reached the correct level for the required pressure of gas. Then tap 1 was gradually opened and gas allowed to enter until the Bourdon gauge pointer returned to its null position.

As a final precaution, it was arranged that the pressure of gas on both sides of the Bourdon gauge and in the main gas line, was identical. This was done by evacuating the gas in the main line to approximately the same pressure as in the reaction vessel. Then, on opening tap 4, the gauge pointer probably moved a small amount, and either by judicious evacuation or admission of air, the pointer was brought back to its original position. In that way, the pressures of gas on either side of tap 1 were identical, hence diminishing any tendency for gas leaks to occur, either into or out of, the reaction vessel.

METHOD OF DETERMINING THE PROGRESS OF THE REACTION.

The way in which the chlorine concentration, and hence the reaction rate, could be determined at any time, followed the method originated by Ritchie and Norrish[1] in their examination of the hydrogen-chlorine photo-reaction.

The great advantage this method possesses is that it does not disturb the equilibrium of the gas system. In certain cases, when the reaction is sufficiently slow, its entire progress can be plotted out as it occurs, - the "graphical" method. In most cases, however, it is necessary to "kill" the reaction at a chosen instant (by addition of sufficient oxygen) and then to determine how far reaction has proceeded - the "method of averaging."

Both modifications of the method depend on the fact that chlorine gas absorbs transmitted light of a suitable wavelength, to a considerable extent, and a relationship exists between the intensity of the incident light absorbed and the corresponding concentration of chlorine present - namely, Beer's Law.

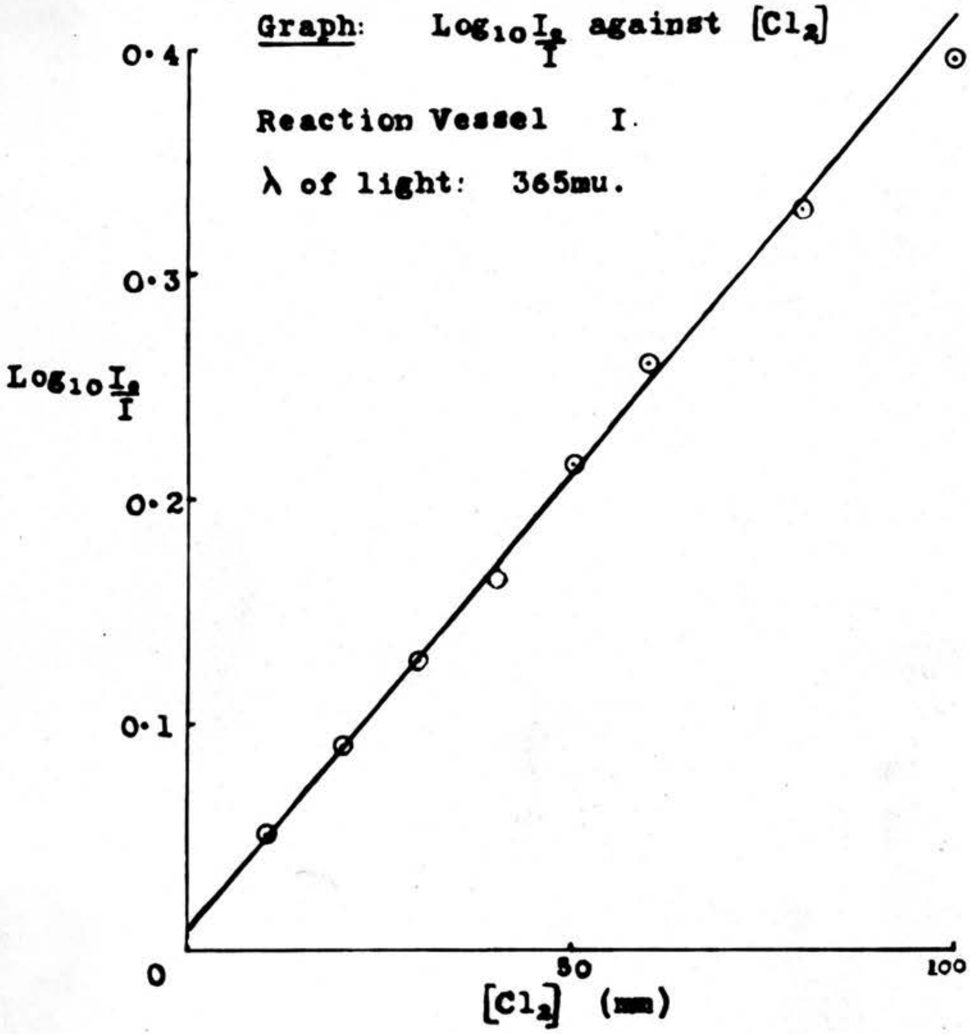
$-\frac{dI}{dc} \propto I$ c — concentration of substance, or pressure of gas.

i.e. $\log \frac{I_0}{I} \propto c$ and $= kc$ I — intensity transmitted, with the absorbing medium present.

or $\log_{10} \frac{I_0}{I} = k'c$ $(k = 2{\cdot}303k')$ I_0 — intensity transmitted, with no absorbing medium present.

Hence, by using suitable monochromatic light and measuring its intensity by means of the photoelectric cell in combination with the galvanometer as previously described, a series of values of $\log_{10} \frac{I_0}{I}$ was obtained for various pressures of chlorine in the reaction vessel. This gave an almost straight line calibration graph, and hence by noting the values of the original intensity I_0 of transmitted light with the reaction vessel empty, and then the transmitted light intensity I with an unknown concentration of chlorine present, the value of $\log_{10} \frac{I_0}{I}$ can be calculated immediately, and the pressure of chlorine in the reaction vessel determined by reading directly from the graph.

Concentrations of chlorine used for calibration ranged from 10 mm to 100 mm for 365 mu light, and 50 mm to 400 mm using 406 mu light. Estimations of chlorine concentration carried out in this way, possessed an experimental error of, normally, not greater than 0.5 mm.

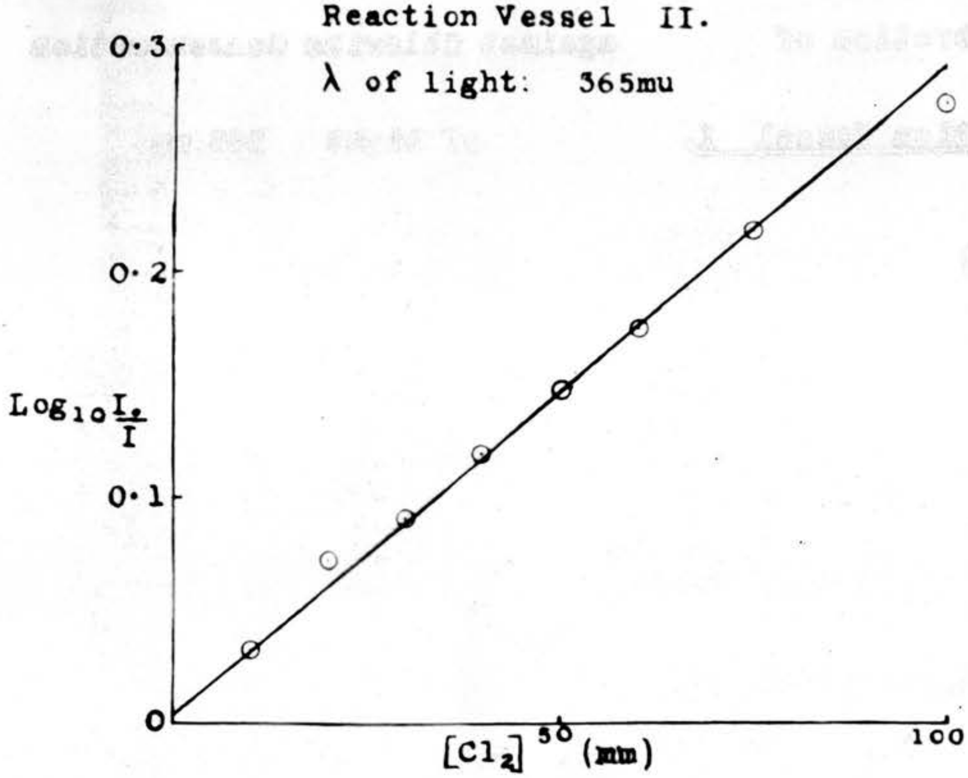


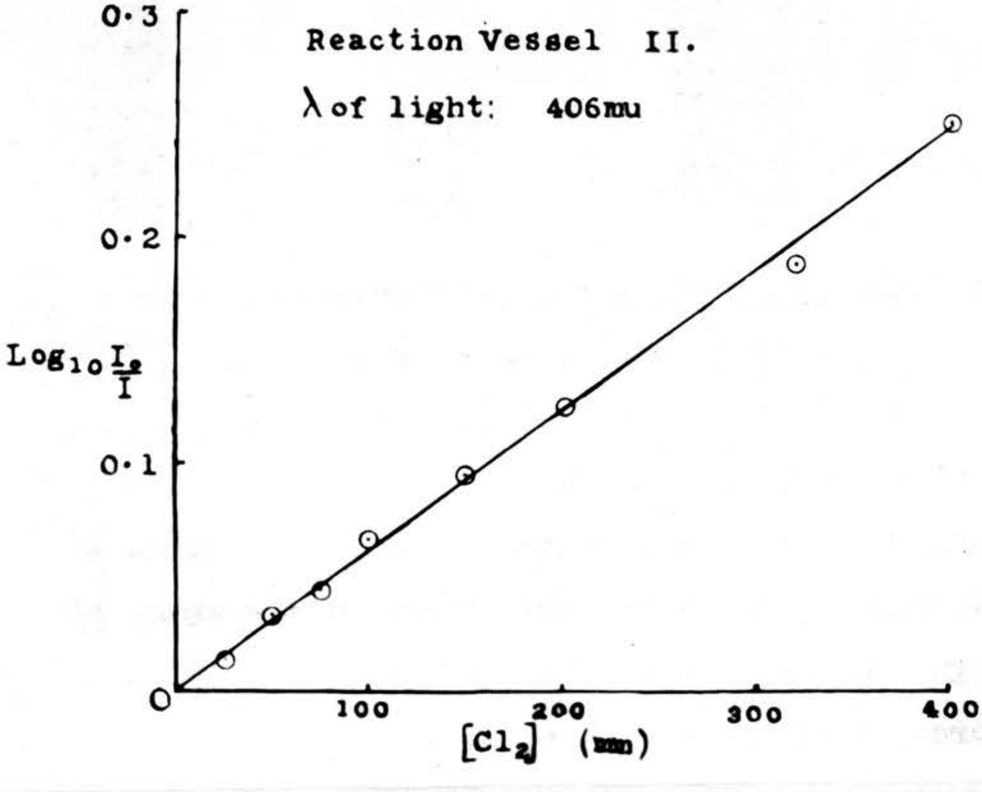
Graph: $\mathrm{Log}_{10}\frac{I_a}{I}$ against $[Cl_2]$

Reaction Vessel I.

λ of light: 365mu.

Graph: $\log_{10}\frac{I_0}{I}$ against $[Cl_2]$





Calibration of $\log_{10}\frac{I_0}{I}$ against Chlorine Concentration.

Reaction Vessel I. λ of Light 365 mu.

$[Cl_2]$ (mm)	I_0 (galv. scale divs.)	I (galv. scale divs.)	$\therefore \log_{10}\frac{I_0}{I}$
10	44.0	39.1	0.0513
20	44.0	35.8	0.0896
30	44.0	32.7	0.1290
40	44.0	30.1	0.1649
50	45.7	27.9	0.2143
60	45.7	25.1	0.2602
80	45.7	21.5	0.3275
100	45.7	18.4	0.3957

Reaction Vessel II.

λ of Light 365 mu.		λ of Light 406 mu.	
$[Cl_2]$ (mm)	$\log_{10}\frac{I_0}{I}$	$[Cl_2]$ (mm)	$\log_{10}\frac{I_0}{I}$
10	0.0315	25	0.0134
20	0.0726	50	0.0331
30	0.0918	75	0.0447
40	0.1202	100	0.0670
50	0.1484	150	0.0962
60	0.1761	200	0.1250
75	0.2195	300	0.1879
100	0.2757	400	0.2516

Correction for the Volume of the Connecting Tubing.

The usual procedure in actual observations was to measure chlorine concentrations after the reaction had been "killed" by the addition of oxygen, — 300 mm in the chlorine-toluene reaction. Hence as a preliminary examination, the effect of the entry of this gas was determined, when simply chlorine itself was present in the reaction vessel.

The procedure was to take the value of I_o, with the reaction vessel empty and then introduce that pressure of chlorine, which was to be taken as the final value at the end of the particular reaction sequence. The value of I was noted, - the transmitted intensity with chlorine present. Hence, reading off the value of $\log_{10}\frac{I_o}{I}$ from the calibration curve should corroborate the pressure of chlorine introduced, as measured by the Bourdon gauge-manometer combination.

Next, the oxygen was introduced slowly into the reaction vessel, and after leaving for a few minutes to allow homogeneous mixing of the gases, the new value of I examined. It was found that slightly less light was now transmitted than previously, due to the "washing" of the chlorine in the connecting tubes into the reaction vessel. The vessel was re-evacuated, and any change in I_o from the first value, noted.

For example:

In observations on the thermal reaction between chlorine and toluene, the initial pressure of chlorine was 30.0 mm, and the final value about 21 mm. 300 mm of oxygen were added to kill the reaction.

Hence, to find the effect of this addition of oxygen, 21 mm of chlorine were introduced into the reaction vessel, 300 mm of oxygen added, and the apparent concentration of chlorine now read off.

Results.

Initial value of I_0 = 39.6 cm. (on the galvanometer scale).

Corresponding value of I on introducing 20.8 mm chlorine = 31.8 cm.

$$\therefore \log_{10}\frac{I_0}{I} = 0.0953$$

From the graph of $\log_{10}\frac{I_0}{I}$ against $[Cl_2]$, this corresponds to 20.6 mm chlorine.

On introducing 300 mm of oxygen,

Altered value of I = 30.9 cm.

Corresponding value of I_0, on evacuation = 39.8 cm.

$\therefore \log_{10}\frac{I_0}{I}$ = 0.1099, corresponding to 24.2 mm chlorine.

∴ Effect of adding 300 mm oxygen to the reaction vessel, containing about 21.0 mm chlorine, is to give an apparent value of the chlorine concentration, 3.6 mm too great.

This procedure was carried out several times, and the average increase in chlorine concentration as measured by the photometric system, was found to be 3.4 mm.

The correction, which it would thus be necessary to apply for each observation, was considered to be too large for accurate measurement. So, in order to reduce the discrepancy between the apparent and real pressures of chlorine present, the glass tubing connecting the ground joint at the reaction vessel to the Bourdon gauge and tap 1 was replaced by capillary tubing. The reaction vessel already possessed a capillary stem.

When similar observations were made after this modification had been carried out, the correction necessary was reduced to 2.0 mm. This value was considered sufficiently small for an accurate correction to be made to the observed chlorine concentration, after addition of inert gas.

Illumination of Gaseous Mixtures.

The two wavelengths of light employed for illumination were 365 mu and 406 mu.

The method has already been described for determining the value of $\log_{10}\frac{I_0}{I}$ for 365 mu light, and hence measuring the concentration of chlorine present in the reaction vessel at any stage. From the same graph of $\log_{10}\frac{I_0}{I}$ against $[Cl_2]$, the value of the relative absorption coefficients of chlorine for either wavelength can be obtained.

At a pressure of 100 mm of chlorine, the actual figures for reaction vessel II, are:-

For 365 mu light: 0·2950

For 406 mu light: 0·0620

The absorption of light of wavelength 365 mu is greater, and the estimation of the intensity of light absorbed, I_{abs}, by a given pressure of chlorine in the reaction vessel, can be readily found by evaluating $\log_{10}\frac{I_0}{I}$ from the graph, and calculating, as in the following example:-

In one observation in reaction vessel I, the chlorine concentration dropped from 50.0 mm at the beginning of the experiment to 40.0 mm at the end. Hence the average pressure of chlorine present is 45.0 mm, and the value of $\log_{10}\frac{I_0}{I}$ (λ= 365 mu) for this pressure is 0.1896.

If the original value of I_0 for the particular filter used is 40.0 cm. on the galvanometer scale, a value of I is calculated from:

$$\log_{10}\frac{I_0}{I} \text{ for } [Cl_2] \text{ of } 45\text{ mm} = 0.1896 = \log_{10}\frac{40.0}{I}$$

$$\therefore \log_{10} I = 1.6021 - 0.1896$$

$$= 1.4125$$

$$\therefore I = 25.85 \text{ cm. on galvan. scale.}$$

$$\text{But } I_{abs} = I_0 - I = 40.0 - 25.85 \text{ cm.}$$

$$= \underline{14.15} \text{ cm on galvan. scale.}$$

In the case of 406 mu light, where the light absorption of chlorine is small, sufficiently accurate values of $\log_{10}\frac{I_0}{I}$ cannot be obtained by direct reading from the graph.

Hence, in such cases, the value of $K = \frac{\log_{10}\frac{I_0}{I}}{[Cl_2]}$ was obtained from the slope of the graph, and to find an accurate value of $\log_{10}\frac{I_0}{I}$ at any given chlorine concentration, the values of K and $[Cl_2]$ were substituted in the above relationship. The value of I_{abs} was then determined as in the case of light of λ = 365 mu.

Evaluation of K:

Reaction vessel II.

Light of λ = 406 mu.

$$\log_{10}\frac{I_0}{I} \propto [Cl_2]$$
$$= K[Cl_2]$$
$$\therefore K = \frac{\log_{10}\frac{I_0}{I}}{[Cl_2]}$$

At 400 mm pressure of chlorine, $\log_{10}\frac{I_0}{I} = 0{\cdot}2500$

$$\therefore K = \frac{0{\cdot}2500}{400}$$
$$= \underline{0{\cdot}000625.}$$

Calibration of Bourdon Gauge.

Before carrying out observations on the Budde Effect in chlorine, a calibration of the Bourdon gauge was necessary to translate the observed pressure effects, measured in scale divisions, to mm of mercury pressure.

The procedure for carrying this out, is as follows:

The apparatus was completely evacuated, and tap 4 closed, thereby isolating the manometer arrangement. Evacuation was continued for some time, and if the original evacuation had been sufficient, no movement of the Bourdon gauge pointer occurred.

The telescope, containing a scale, reading from zero to 100, was focussed so that the 50 mark on the scale coincided with one edge of the gauge pointer. Air was now carefully introduced through tap 1 into the reaction vessel, until the gauge pointer lay between the zero and 10 mark on the scale.

The telescope stand was again adjusted to bring the gauge pointer once more back in focus to the 50 mark on the scale, and the air in the reaction vessel evacuated. The pointer moved to about the 90 mark on the telescope scale. The apparatus was now ready for the actual calibration to be made.

The readings on the standard and the experimental manometers were taken. Air was slowly introduced through tap$_{\alpha}$ and the mercury in the experimental manometer dropped slightly. Concurrently, the pointer of the Bourdon gauge moved, and when it reached about the 60 mark on the telescope scale, tap$_{\alpha}$ was closed, and accurate readings of the manometer pressures and position of the gauge pointer carried out.

The procedure was repeated for approximate readings of 30 and 5 divisions on the telescope scale, along with corresponding manometer measurements.

At either end of the scale, the telescope was slightly out of focus, but, by using the method described, this is kept to a minimum, and the scale can be read to 0.1 of a division around the 50 mark, and 0.2 of a division near the 0 and 100 marks.

This is the procedure when the reaction vessel is under a vacuum. A similar calibration of the gauge was next carried out when the reaction vessel contained gas at various pressures, - 20 mm, 40 mm, and 60 mm, of mercury. The sensitivity of the gauge differed very little in each case.

By this method, the pressure of mercury corresponding to one division on the telescope scale can be found.

Calibrations were carried out for two gauges of differing sensitivity. Data on following pages.

Gauge I.

Approx. Gas Pressure (mm Hg)	Standard Manometer Reading. (mm Hg)	Expt. Manometer Reading. (mm Hg)	Telescope Scale Reading. (divisions)	Corresponding Pressure Difference (mm Hg)	Corresponding Pressure Difference (telesc. sc. divs.)	One scale division corresponds to mm Hg pressure.
750	754.9	754.9 753.0 750.7 748.7	96.7 68.5 35.6 4.4	1.9 2.3 2.0	28.1 32.9 31.2	0.069 0.070 0.066
600	756.4	607.3 605.4 603.4 601.4	92.8 66.2 35.9 7.0	1.9 2.0 2.0	26.6 30.3 28.9	0.070 0.067 0.068
400	758.5	396.3 394.2 392.0 390.1	95.2 62.7 32.6 5.8	2.1 2.2 1.9	32.5 31.1 26.8	0.066 0.071 0.069
200	760.2	210.4 208.9 206.9 204.7	90.6 67.2 38.7 8.7	1.5 2.0 2.2	23.4 28.5 31.0	0.067 0.070 0.072

Gauge I possessed an average sensitivity of 0.069 mm per telescope scale division.

Gauge II.

Approx. Gas Pressure (mm Hg)	Standard Manometer Reading. (mm Hg)	Expt. Manometer Reading. (mm Hg)	Telescope Scale Reading. (divisions)	Corresponding Pressure Difference (mm Hg)	Corresponding Pressure Difference (telesc. sc. divs.)	One scale division corresponds to mm Hg pressure.
750	752.1	752.1	90.2	0.9	27.5	0.034
		751.2	62.7	0.9	24.1	0.037
		750.3	38.6	1.0	29.2	0.036
		749,3	9.4			
600	753.5	604.9	95.6	1.0	27.4	0.038
		603.9	68.2	1.2	34.5	0.035
		602.7	33.7	1.0	28.5	0.035
		601.7	5.2			
400	755.7	404.2	93.6	0.9	29.2	0.037
		403.3	64.4	1.1	32.3	0.033
		402.2	32.1	1.0	28.9	0.036
		401.2	3.2			
200	757.6	206.2	97.8	1.1	29.1	0.039
		205,1	68.7	1.2	33.5	0.036
		203.9	35.2	0.9	26.6	0.032
		203.0	8.6			

Gauge II possessed an average sensitivity of 0.036 mm per telescope scale division.

The previous account of the experimental procedure suffices for the Budde Effect observations in section I.

The following pages describe the arrangements necessary to measure the rate of the thermal and photoreactions reported in sections II and III.

EXPERIMENTAL MEASUREMENT OF QUANTUM EFFICIENCY, AND CALIBRATION OF REACTION VESSELS.

In the subsequent investigations of the photo-chlorination of toluene and methane, values of the rate of reaction were found for given concentrations of reactants and under standard condition of illumination.

The corresponding quantum efficiency, γ, of chlorine can be deduced from an equation of the type:

$$\gamma_{Cl_2} = \frac{\Delta Cl_2}{t \times I_{abs}}$$

where ΔCl_2 = the change in the chlorine concentration at the beginning and end of the observation.

t = the time in seconds.

I_{abs} = the intensity (in quanta) of the light absorbed per second.

Obviously, a value of I_{abs} is necessary before suitable calculations can be made. A measure of its size is given immediately from the galvanometer deflection, in combination with the graph of $\log_{10} \frac{I_0}{I}$ against $[Cl_2]$, as previously described. However, this is merely a relative value, and to obtain values of γ in molecules per quantum of absorbed light, the factor necessary for converting I_{abs} in galvonometer scale divisions to absolute units, light quanta per second, must be found.

In the original investigation of Ritchie and Norrish,[1] in which a thermopile was used to measure the light intensity, the absolute measurement of I_{ab} was found by obtaining the value, first, of the number of quanta per second falling on the thermopile, and then estimating how much light was lost in various ways in its passage from the rear-window of the reaction vessel, through the thermostat liquid, water-jacket window, and air, before reaching the thermopile, and also by reflection from certain metallic parts of the thermopile itself.

Hence, an absolute value of I_{ab}, in quanta per second, was obtained for the optical system used, and this value was employed in their calculations of quantum efficiency. One series of such calculations concerned the relationship between the quantum efficiency of formation of HCl and the pressure of oxygen present.[3] In a later paper on oxygen-rich mixtures, using a similar technique, Ritchie[4] employed certain of these quantum efficiency determinations in order to calibrate the optical system, and hence obtained absolute values of quantum efficiency from the relative figures measured. Obviously, this procedure will only yield completely accurate results, if the original and later systems are identical in all respects. Despite the slight dissimilarity in the apparatus used, and even in the surfaces of the reaction vessels, - one composed of quartz, the other of soft glass - the procedure was justified by the close agreement between the theoretical and actual values of the results obtained. This procedure was also adopted in the observations of Ritchie and Taylor,[5] and found once more to be entirely justified.

In the present observations, this method was again employed to calibrate the optical system and obtain quantum efficiencies in absolute units. Details of the procedure are given in the following section.

Procedure.

The method followed in order to calibrate the reaction vessels was similar to the general technique whereby observations of the reaction rates between chlorine and toluene, and chlorine and methane were later carried out. Hence, as a general example, the procedure is given in detail. The vessels were calibrated for both wavelengths employed.

The whole apparatus was thoroughly evacuated, the manometer isolated by closing tap m, and evacuation continued further. Taps 1 and 4 were now closed, at the same time opening tap m once more, thereby isolating the Bourdon gauge-manometer combination and the reaction vessel. The relevant tap was opened to evacuate the space above the solid chlorine in tube c for 10 minutes, after which the chlorine was again isolated, and allowed to liquify by removal of the surrounding liquid oxygen. When the chlorine was almost completely liquified, its vapour, and any trace of foreign gases, were drawn off several times by evacuation for a few seconds.

Tap 1 was now closed, the main gas line filled with chlorine, and the reaction vessel "washed" with the gas several times. It was finally filled with 50 mm of chlorine by the method described previously. (page 11).

Before entering the chlorine, it was customary to note the value of I_0 on the galvanometer scale, and the value of I, the transmitted light intensity, after 50 mm of chlorine had been added. In that way, check was kept on the $\log_{10}\frac{I_0}{I}$ against $[Cl_2]$ graph, and any slight variation immediately recorded.

The main gas line was now completely evacuated for some ten minutes, during which time the chlorine in the reaction vessel was illuminated to destroy any possible inhibitors present.

The next gas to be introduced into the reaction vessel was oxygen. In the calibration using 365 mu light, due to its greater absorption by chlorine than with 406 mu light, and hence the correspondingly greater rate of reaction, 50 mm of oxygen were added. With 406 mu light, 10.1 mm oxygen were sufficient to give a measurable reaction rate.

Tap 1 was closed, purified oxygen introduced into the main gas line, and then evacuated for about 30 seconds, to remove any traces of foreign gas. Again, the main gas line was filled with oxygen, and the correct amount introduced into the reaction vessel. Illumination of the vessel was continued.

The oxygen was evacuated completely from the main gas line, and then after a preliminary "washing" with hydrogen, filled with the gas. After taking care to cut off illumination of the reaction vessel, 50 mm of hydrogen were introduced into it.

It was customary, at this stage, to leave the reaction mixture for some minutes to mix thoroughly. It was noticed empirically that the results were more reproducible when this precaution was observed.

Illumination of the reaction vessel and gas mixture was now begun, and timed with a stop-watch. In the case of 365 mu light, the time taken, for the light filter used, was about one-fifth of that for a 406 mu light filter, using a gas mixture of 50 mm chlorine + 10.1 mm oxygen + 50 mm hydrogen. In either case, this reduced the chlorine concentration by about 15 mm, i.e. 30% of the original quantity of chlorine present as demanded if the values of the corresponding quantum efficiencies deduced by Norrish and Ritchie[3] are to hold valid. During this period, the photo-cell was cut off from illumination by closing the shutter between the reaction vessel, and the cell itself.

A few minutes before ceasing illumination of the gas mixture, this shutter was opened and a value of I, the transmitted light intensity, read off from the galvanometer scale.

It was considered unnecessary, in these observations, to add additional oxygen to "kill" the reaction, due to its already slow rate. In other observations, usually in oxygen-free systems, in which this procedure was necessary, the method adopted was to cut off illumination, evacuate the main gas line, introduce the oxygen to the reaction vessel, adding sufficient to "kill" the reaction and allow a galvanometer reading to be taken. Again, it was customary to leave the reaction mixture for a short time to attain equilibrium, before illuminating to read the value of I.

In either case, after I had been determined, the whole apparatus was quickly evacuated (without again cutting off illumination) and a final value of I_o determined.

However, if for illumination, 365 mu light of too low an intensity was being used to allow chlorine concentrations to be measured photometrically, or if the light was of a wavelength other than 365 mu, it was necessary to change to an appropriate 365 mu light filter before determining I, and later I_0.

Hence a measure was obtained of the concentration of chlorine remaining in the reaction vessel at the end of the observation.

A typical example of how the relative value of the quantum efficiency was obtained, and further, how the corresponding absolute value, in molecules per quantum, was derived, is given below.

Data. Reaction Vessel I.

λ of light used - 365 mu.

Initial Concentration of Chlorine - 50.0 mm.

" " " Oxygen - 50.0 mm.

" " " Hydrogen - 50.0 mm.

Time of illumination - 20 mins. = 1200 seconds.

Preliminary Check. Before introducing the chlorine into the reaction vessel, the intensity of light transmitted through the empty vessel, I_0, as measured by the galvanometer, was found to be 30.0 cm.

After 50 mm of chlorine, as measured by the manometer, had entered the vessel, the new intensity of the light transmitted, I, was 18.3 cm on the galvanometer scale.

Hence by the method described on page 15,

$$\mathrm{Log}_{10}\frac{I_0}{I} = \log_{10}\frac{30.0}{18.3} = 04771 - 0.2625 = 0.2146$$

and this corresponds on the $\log_{10}\frac{I_0}{I}$ against $[Cl_2]$ graph to 50.1 mm, - within the experimental error.

Procedure. The oxygen and hydrogen are now added and illumination continued for 20 minutes.

The value of I at the end of that period was = 21.4 cm on the galvanometer scale, and, on evacuation, the corresponding value of I_0 was again 30.0 cm.

Hence the concentration of chlorine remaining in the reaction vessel was found, as previously:-

$$\mathrm{Log}_{10}\frac{I_0}{I} = \log_{10}\frac{30.0}{21.4} = 0.1467$$

corresponding to a chlorine concentration of 35.0 mm.

Subtracting 2.0 mm for the ~~value~~ volume of the capillary tubing, gives a final value of 33.0 mm of chlorine.

The pressure of chlorine which reacted during the observation = 50.0 - 33.0 mm.

$\Delta\ Cl_2 = 17.0$ mm.

Calculation of I_{abs} (Relative Value.)

The actual pressures of chlorine in the reaction vessel at the beginning and end of the observation, due to the effect of adding other gases, were 52.0 and 35.0 mm.

∴ The average value of the chlorine concentration throughout the observation was 43.5 mm.

$\therefore$ The average value of the light absorbed throughout the observation can be found by the method on page 20.

Hence I_{abs} = 10.40 cm on the galvanometer scale.

<u>Calculation of Quantum Efficiency</u> (Relative Value)

$$\gamma_{HCl} = \frac{2 \times \Delta Cl_2}{t \times I_{abs}}$$

$$\frac{2 \times 17.0}{1200 \times 10.40}$$

$$\underline{0.002725}$$

It was by a method, analagous to this, that relative values of γ were calculated in the reactions between chlorine and toluene, and chlorine and methane.

<u>Calculation of Absolute Values</u>.

In their original observations, with the same gas reaction mixture as above and using light of wavelength 365 mu, Norrish and Ritchie[3] found the absolute value of the quantum efficiency of HCl to be 125 molecules per quantum.

Hence, introducing a constant "k" into the equation, thus:

$$\gamma_{HCl} = K \frac{2 \times \Delta Cl_2}{t \times I_{abs}}$$

and evaluating "k", we have an immediate method of conversion of quantum efficiencies in the above equation from relative units, as calculated previously, to absolute units, - molecules per quantum of light absorbed.

In the example taken,

$$\gamma_{HCl} = 125 \text{ molecules per quantum} = K \frac{2 \times 17.0}{1200 \times 10.40}$$

$$\therefore K = \underline{45,870.}$$

With the hydrogen-chlorine reaction, the final product of illumination is known to be HCl. However, in the calculation of quantum efficiencies in the subsequent observations, where the actual products formed are not of a definite nature, it is more convenient to be able to convert values of I_{abs} in cm on the galvanometer scale to quanta of light absorbed per second.

The method is first to convert mm of chlorine present in the reaction vessel to the actual number of molecules.

Using the data in the previous example, since 22.4 litres of gas at 760 mm pressure and 273°A contain 6.06×10^{23} molecules, then 17.0 mm of chlorine at 298°A, contained in reaction vessel I of volume 31.35 ml, will contain

$$6.06 \times 10^{23} \times \frac{31.35}{22,400} \times \frac{273}{298} \times \frac{17.0}{760} \text{ molecules}$$

$$= 1.738 \times 10^{19} \text{ molecules.}$$

Rearranging the previous equation to obtain I_{abs}

$$\therefore I_{abs} = \frac{2 \times 1.738 \times 10^{19}}{125 \times 1200 \times 10.4}$$

$= 2.229 \times 10^{13}$ quanta per second corresponding to 1 cm on the galvanometer scale.

Obviously, the values of "k" and I_{abs} in absolute units, will vary with the arrangement of the system of illumination, and, in particular, with each reaction vessel.

To find the absolute values of γ throughout this investigation, the chlorine concentration was converted each time to molecules, and the value of I_{abs} to quanta per second, before substitution in the general equation.

Calibrations were carried out for the 2 reaction vessels used in the examination of the chlorine-toluene and chlorine-methane reactions: in the case of reaction vessel I, for light of wavelength 365 mu; and for reaction vessel II, for wavelengths of 365 mu and 406 mu.

In the latter case, due to the much smaller absorption of light of λ = 406 mu by chlorine, the gas mixture used, consisted of 50 mm chlorine + 10.1 mm oxygen + 50 mm hydrogen. The absolute value of the of HCl in this case was found by Norrish and Ritchie[3] to be 560 molecules per quantum of light absorbed.

Reaction Vessel I.

Volume 31.35 ml. λ of Light = 365 mu.

$[H_2]$ mm.	$[Cl_2]$ mm.	$[O_2]$ mm.	ΔCl_2 mm.	I_{ab} cm.	t secs.	$\gamma \times 10^{-3}$ relative.	$k \times 10^4$.	$I_{ab} \times 10^{13}$ absolute
43.5	43.5	50.0	17.0	10.4	1200	2.73	4.59	2.23
42.9	40.8	50.9	18.4	9.5	1380	2.80	4.45	2.30
41.6	40.8	50.0	18.5	11.7	1200	2.64	4.74	2.16
41.4	41.4	50.0	17.3	9.9	1200	2.91	4.29	2.38
41.5	41.5	50.1	17.0	10.6	1200	2.67	4.68	2.19
41.7	41.7	50.4	17.2	10.5	1200	2.73	4.58	2.23

Average value of "k" = $\underline{4.56 \times 10^4}$
Average value of I_{ab} in quanta per sec. = $\underline{2.25 \times 10^{13}}$, corresponding to 1 cm on galvanometer scale.

Reaction Vessel II.

Volume 21.74 ml. λ of Light = 365 mu.

$[H_2]$ mm.	$[Cl_2]$ mm.	$[O_2]$ mm.	ΔCl_2 mm.	I_{ab} cm.	t secs.	$\gamma \times 10^{-3}$ relative.	$k \times 10^4$.	$I_{ab} \times 10^{13}$ absolute
42.8	42.8	50.0	14.4	10.6	2000	1.36	9.20	0.771
42.6	42.7	50.0	14.7	10.6	2000	1.39	9.01	0.787
42.9	42.9	50.1	14.2	10.6	2000	1.34	9.33	0.760

Average value of "k" = $\underline{9.18 \times 10^4}$.
Average value of I_{ab} in quanta per sec. = $\underline{0.773 \times 10^{13}}$, corresponding to 1 cm on galvanometer scale.

Reaction Vessel II.

Volume 21.74 ml. λ of Light = 406 mu.

$[H_2]$ mm.	$[Cl_2]$ mm.	$[O_2]$ mm.	ΔCl_2 mm.	I_{ab} cm.	t secs.	$\gamma \times 10^{-3}$ relative.	$k \times 10^4$.	$I_{ab} \times 10^{13}$ absolute
43.6	43.4	10.1	13.2	1.00	10,680	2.47	22.65	0.313
44.0	44.1	10.1	11.3	0.80	10,680	2.65	21.17	0.335
43.3	43.4	10.1	13.3	0.99	10,740	2.50	22.39	0.317

Average value of "k" = $\underline{22.07 \times 10^4}$
Average value of I_{ab} in quanta per sec. = $\underline{0.322 \times 10^{13}}$, corresponding to 1 cm on galvanometer scale.

Calibration of Filters.

In observations in which the quantum efficiency is measured at different intensities of absorbed light, it is necessary to gradually "scale down" the incident light intensity.

In the previous investigations of Ritchie and Norrish,[6] and Ritchie and Taylor,[5] this was done by interposing a number of blue glass plates, after first filtering to secure monochromatic light. In the present observations, the materials examined for use as filters, were various blue glass plates, $\frac{1}{2}$- and $\frac{1}{4}$-tone filters, and another thick 365 mu filter. Their relative intensities are given later.

Bodenstein[7] has criticised the use of such blue glass plates on the following grounds. Ritchie and Norrish[6] had shown that, in oxygen-free systems, the rate of HCl formation was not proportional to the first power of I_{abs}, but tended to become proportional to the square root of I_{abs}, at low values of I_{abs}. Bodenstein explained this tendency by assuming that the alleged monochromatic nature of the filter is not borne out in practice. Hence, he estimated the proportions of light of various wavelengths which would be transmitted through blue glass plates, and contrived to prove that this accounted for the tendency for the exponential "n" of I_{abs}, to change from unity to 0.5.

One method to test the validity of this criticism, from the point of view of the kinetics, is to examine a reaction in which the rate is known to be proportional to the first power of the intensity of absorbed light. Then if, on cutting down the light intensity, using the very varied filters under examination, the rates of the reaction remain proportional to the corresponding first power of I_{abs}, it can be concluded that these extra filters do not, as suggested, affect the monochromatic nature of the light, and are not responsible for the power of I_{abs} being less than unity, as previously found.

Norrish and Ritchie[3] proved, in agreement with all other workers, that the rate of the photo-reaction between hydrogen and chlorine, in the presence of 10.1 mm and 50 mm of oxygen, was directly proportional to the first power of I_{abs}, and hence that the quantum efficiency was independent of the value of I_{abs}.

$$\frac{d[HCl]}{dt} \propto I_{abs}$$

$$\gamma_{HCl} = k\,\frac{2 \times \Delta Cl_2}{t \times I_{abs}}$$

$$= 560 \text{ molecules per quantum}$$

using light of $\lambda = 365$ mu, for the gas mixture containing ~~50~~ 10·1 mm oxygen.

Hence, it is seen that if the value of "k" in the above equation remains the same for varying intensities of incident light, then the criticism of Bodenstein will no longer be valid, and the extra glass plates used, do not experimentally affect the wavelength of the light.

	Filter Combination.	Relative Intensity.
I.	Chance filter 18a (1 mm thickness).	381
II.	Chance filter 18a (1 mm thickness) + 3 blue glass plates.	222
III.	Chance filter 18a (1 mm thickness) + 2 blue glass plates + $\frac{1}{4}$-tone filter.	37
IV.	Chance filter 18a (1 mm thickness) + $\frac{1}{4}$-tone filter + $\frac{1}{2}$-tone filter.	19
V.	Chance filter 18a (1 mm thickness) + Chance filter 18a (2 mm thickness)	7

Reaction Vessel I. λ of Light = 365 mu.

Filter Combination.	$[H_2]$ mm.	$[Cl_2]$ mm.	$[O_2]$ mm.	ΔCl_2 mm.	I_{abs} cm.	t secs.	$\therefore k \times 10^4$
I	42.8	42.8	10.08	14.5	9.3	240	4.31
II	(42.0	42.0	10.1	16.0	5.0	480	4.20
	(42.2	42.2	10.1	15.7	5.0	480	4.28
III	42.6	42.6	10.1	14.8	0.96	2400	4.36
IV	41.8	41.8	10.1	16.5	0.51	5100	4.41
V	43.3	43.3	10.1	13.5	0.236	8100	3.965

It is concluded that the effect of altering the value of I_{abs} 40-fold by the use of various glass sheets, does not materially alter the value of "k".

Hence the quantum efficiency of the gas mixture examined is independent of I_{abs}, and Bodenstein's contention that the use of glass sheets, in changing I_o and I_{abs}, accounts for the variation of the exponential "n" and of the quantum efficiency of oxygen-free mixtures of hydrogen and chlorine cannot be conceded for the present conditions.

Part 1. THE BUDDE EFFECT IN CHLORINE.

Introduction.

The conception that a modification of chlorine other than the chlorine atom or di-atomic chlorine molecule, might exist, has been held for many years. The actual form which this modification of chlorine would take, has varied according to the grounds on which it has been postulated.

The two main forms suggested have been:-

(a) a molecule consisting of three atoms of chlorine.

(b) an electronically-excited form of chlorine, either molecule or ion.

A number of investigations have been carried out, in which chlorine gas was submitted to various physical processes but in no case, has any experimental evidence been produced, pointing directly to such particles, although their presence would account for certain observations.

The question has arisen in an acute form in recent years due to the difficulty of adequately expressing the kinetics of photo-chemical reactions, such as the hydrogen-chlorine photo-reaction, without the assumption of some particle of this kind.

In connection with an investigation of the Budde Effect in chlorine by Ritchie and R.L. Smith,[8] a phenomenon was observed not previously recorded, which might be ascribed to a new modification of chlorine. It is this particular circumstance that has been further examined.

(a) Probably the first allusion to a peculiar condition in chlorine was made by Draper[9] in 1843, when he reported that "chlorine gas which has been exposed to the daylight or to sunshine, possesses qualities which are not possessed by chlorine made and kept in the dark. It acquires from that exposure the property of speedily uniting with hydrogen gas. This new property arises from its having absorbed tithonic rays, corresponding in refrangibility to the indigo. The property thus acquired is not transient, like heat, but permanent."

In this particular case, Burgess and Chapman[10] demonstrated that the reactivity of chlorine by illumination, as shown by an accelerated rate of photoreaction with hydrogen, was due, not to any new substance produced, but simply to the destruction of impurities already present. However, the suggestion was made that at the same time, activation of the chlorine may also take place in some way.

Other early work by Rücker[11] and Berthelot[12] pointed to a peculiar condition in chlorine. The ratio $\frac{C_p}{C_v}$ for chlorine, (identical to the modern figure) when substituted into a formula relating it to the number of atoms in the gas molecule, gave the value of three atoms per molecule, and the possibility of a chlorine molecule of formula Cl_3 was considered. It was alternatively suggested that the value might be due to the two atoms being held only loosely together.

When the production of very pure chlorine became possible, the question of its activation, either under the action of light or of an electric discharge, received much attention.

Mellor[13], repeating Draper's original experiment of illuminating chlorine, found, on the other hand, no increased reactivity of chlorine. He also studied the effect, previously examined by Vernon[14] and Shenstone[15], of passing chlorine and mixtures of chlorine and hydrogen chloride through an ozoniser, and corroberated that no unusual phenomenon occurred.

A measurement of the degree of activation of chlorine by its reaction with benzene, was carried out by Russ[16], after exposing chlorine simultaneously to an electric discharge and light. It was also found that the effect of drying the chlorine decreased the degree of activation.

However, this use of benzene was adversely criticised by Foster[17] in a paper, denying the activation of chlorine by the electric discharge, and showing that no change in its density, before and after the action of the discharge, could be detected.

A more thorough investigation of the effect of a silent electric discharge on carefully-purified chlorine, at a temperature just above its B.P., was made by Briner and Durante.[18] Their experimental arrangements could have detected a very slight volume change, but none was observed. The activation of chlorine, noted by Russ,[16] was attributed to the formation of ozone or oxides of chlorine.

A different mode of attack on the subject was made by Kümmell and Wobig.[19] They determined the vapour density of chlorine, under the influence of light, and found that it had a value 1% higher than in the dark. This would suggest, not a dissociation, but a polymerisation, under the influence of light.

In an attempt to differentiate between a true activation of chlorine, as against the mere destruction of impurities present in the gas, Bodenstein and Taylor[20] carried out experiments to determine how long the apparent activity, produced by illuminating chlorine, persisted. Chlorine was illuminated, then mixed with hydrogen in a darkened vessel, and the mixture examined for hydrogen chloride. It was concluded that the chlorine had completely lost any activity in 1/1600th of a second, and that statements that activated chlorine possessed a long life, are based on measurements involving impure gases, the so-called activity being due to other causes.

Another thorough investigation of the problem was undertaken by Wendt, Landauer, and Ewing.[21] Repeating the original experiments of Draper, they confirmed that chlorine, illuminated by sunlight, does react with hydrogen in the presence of light more rapidly than non-illuminated chlorine. The effect was persistent (still present to a small extent, after 24 hours), but not permanent (it had disappeared after several days). This can, however, be explained by the destruction of inhibitors through illumination, followed by their gradual regeneration. The same effect was noticed, on illuminating with a 3000-watt Bovie mercury lamp.

They then examined the effect of submitting chlorine to illumination and an electric discharge followed by admixture with hydrogen in the dark, as carried out by Bodenstein and others. It was confirmed that, in no case, was any hydrogen chloride formed, and hence concluded that any "activated" form of chlorine would have a life of certainly less than a second, probably less than 0.01 second, the time interval between illumination and mixture with hydrogen in the above experiments.

Venkataramaiah[22] claimed, in 1922, not only to have prepared active chlorine in four ways - by the action of an ordinary electric discharge, a silent electric discharge, ultra-violet light, and thermally, but also to have examined its chemical properties, and concluded that it was more reactive than un-treated chlorine. In agreement with Kümmel and Wobig[19], he found that chlorine contracted in volume on activation, suggesting an allotropic modification of chlorine, and not the formation of atoms.

Following similar lines, Schaum and Feller[23] submitted chlorine to the action of light and a silent electric discharge simultaneously. They carried out experiments on a series of organic compounds, including toluene, using ordinary chlorine and chlorine as treated above. Greater reactivity was claimed for the treated chlorine.

An attempt to detect a change in the physical properties of chlorine, when strongly illuminated, was made by W. Taylor[24]. By analogy with the method used by Smith[25] for detecting active nitrogen, the refractive index of chlorine was examined using sodium D light, and again on strong illumination with light of frequencies on the ultra-violet side of $\lambda = 4990$ Å. It was calculated that any change in the interference bands would be small, and the most delicate methods of detection, necessary. The results of several experiments were quite negative.

The presence of an unstable catalyst in the photo-reaction between hydrogen and chlorine was postulated by Chapman and Griggs[26], on the basis that combination of the gases takes place more rapidly in a narrow capillary tube than in one of wider diameter. Using the actinometer method, various conclusions regarding the rate of formation and disappearance of the catalyst were put forward, but the results gave no indication of the actual nature of the catalyst.

A comprehensive examination of the activation of chlorine was carried out by Willey and Foord,[27] and the conclusion reached that "the phenomena are very probably due to a trace of atomic chlorine, whose behaviour is markedly dependent upon the surface characteristics of the vessel." Doubt is cast on the results of Venkataramaiah.[22]

Under the action of a silent electric discharge, chlorine was found to expand to the extent of 1 : 2000, possibly due to a small concentration of chlorine atoms or to a small temperature change.

Absorption spectra of chlorine, before and after the action of electric discharges, were examined over the range 5000 - 2100 Å. No additional absorption to that of normal chlorine was found.

Various reactions with ordinary and treated chlorine were carried out. In reactions with ferrous salts, oxalic acid, acetic acid, methane, hydrogen and dyes, the results did not allow definite conclusions to be drawn between the action of ordinary and treated chlorine.

The amount of hydrogen chloride formed, by the action of chlorine on water, was found to be three times greater, when the chlorine had been previously passed through a spark discharge.

In the case of the action on liquid toluene, no difference occurred in the amount of substitutional chlorination, but a 10% increase in the total chlorination was recorded, using sparked chlorine.

It is with the action on benzene, as previously carried out by Russ[16], that the most evidence for the activation of chlorine arises. The use of a silent electric discharge gave more convincing results than the spark discharge, and a definite increase in the total chlorination of benzene was observed. The effect of adding impurities, such as oxygen, nitrogen, or air, on the amount of activation of chlorine was examined, by measuring the action on benzene. Only in the case of air did chlorine, previously passed through a spark discharge, give increased reaction with benzene.

The question arose as to whether the increased reaction was due to active chlorine or to some compound of nitrogen and oxygen, or nitrogen, oxygen and chlorine. Such compounds were tested to find if their presence hastened the reaction between chlorine and benzene, but no increase was observed.

The effect of the irradiation of chlorine was also examined. No activity whatever was observed, as measured by the reaction with benzene, after the simple irradiation of chlorine. Also, the activity of chlorine was not further increased by irradiation of chlorine, before passage through the silent discharge, or irradiation during the actual discharge. Irradiation, after passage through a discharge, gave rise to anomalous results, sometimes an increase, sometimes an actual decrease in activity.

Recently, a new effect has been noted by Joshi and Deo[28], on passing an electric discharge through certain gases in a Siemens' ozoniser. Applying simultaneous irradiation, an instantaneous diminution in the conductivity was observed, the effect being most noticeable in the halogens, especially in chlorine.

Two explanations have been put forward. Parshad[29] considers that the radiations, falling on the chlorine gas, excite it to higher vibrational and electronic states, with a corresponding decrease in the dielectric constant. However, Sahay[30] suggests that the decrease in conductivity is due to some mechanism by which a recombination of the ions takes place, on irradiation.

It must be concluded that, in the empirical investigations so far carried out, the evidence for the abnormal reactivity of chlorine in certain circumstances is more probably due to such causes as the presence of atomic chlorine, surface action, and inhibitors, than to any hypothetical particles.

(b) In connection with the kinetics of the hydrogen-chlorine photo-reaction, it has been found that the presence of a particle such as the Cl_3 molecule, would allow a more satisfactory interpretation of the reaction mechanism.

Nernst[31] proposed the chain mechanism as the basis of the photo-chemical reaction between hydrogen and chlorine, the only forms of chlorine present being chlorine atoms and di-atomic chlorine molecules.

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$Cl + H_2 \longrightarrow HCl + H$$

$$H + Cl_2 \longrightarrow HCl + Cl$$

It was Göhring[32] who first introduced the Cl_3 molecule into his reaction scheme. Thirty-four possible reactions occurring in the system are listed, nine of which concern the Cl_3 molecule.

The basic equation is

$$Cl + Cl_2 \longrightarrow Cl_3$$

and the two other equations of importance are

$$Cl_3 + H_2 \longrightarrow 2HCl + Cl$$

$$Cl_3 + O_2 \text{———} ClO_2 + Cl_2$$

In his mechanism, Thon[33] considers that the reaction is brought about by Cl atoms and Cl_3 molecules, rather than activated Cl_2 molecules. This view is supported by the fact that no reaction occurs in yellow-orange or orange-red light, i.e. light of a wavelength, of which there is no question of the dissociation of molecules to atoms. An analagous expression to Thon's for the rate of reaction was obtained by Cremer,[34] who also included the Cl_3 molecule in her scheme of reaction.

On quantum-mechanical grounds, Rollefson and Eyring[35] showed that molecules of the halogens of the type X_3 possess a comparatively long life at room temperatures. By assuming a value of the entropy change for the reaction

$$X + X_2 \longrightarrow X_3$$

and applying the values deduced of the heat content change, corresponding values of the equilibrium constant, Kp, for the above reaction were obtained at various temperatures, and hence, it was easily shown that at room temperature, the principal molecule other than X_2, is X_3, but at high temperatures, is X. The concentration of X_3 calculated is of a reasonable experimental size.

Ritchie and Norrish[6], examining the photosynthesis of hydrogen chloride in the oxygen-free system, give three alternative explanations of the mechanism of recombination of chlorine atoms. Instead of combination of the atoms, with or without a triple collision (see later), one mechanism stipulates that every Cl atom liberated reacts to form Cl_3. These, in turn, may react

$$2Cl_3 \longrightarrow 3Cl_2$$

without the necessity of a triple collision.

In their experiments on the same reaction in which the pressure of hydrogen is low compared with that of chlorine, Craggs and Allmand[36] found that values of the quantum efficiency were 30 - 40% less for ultra-violet light than for visible light, and this was suggested as being due to the formation of Cl_3 molecules at a concentration higher than under normal conditions of illumination.

In these experiments, the chains are almost entirely broken on the walls by adsorption. Comparison of the quantum yields with the rates of diffusion of chlorine atoms to the walls, shows that the efficiency of the walls in removing chlorine atoms is very small. However, one might expect Cl_3 molecules (due to their greater size) to be adsorbed more readily, resulting in a shorter chain length, and hence a smaller value of the quantum efficiency.

The assumption[37] of Cl_3, present in equilibrium concentration as given by the equation:

$$K = \frac{[Cl_3]}{[Cl]\,[Cl_2]}$$

enabled a satisfactory explanation of the effect of normal light intensity on the reaction, and explains the retarding effect of chlorine.

The reactions are assumed:

$$Cl + Cl_2 \longrightarrow Cl_3 \qquad (1)$$

$$Cl_3 \longrightarrow Cl + Cl_2 \qquad (2)$$

$$2Cl_3 \longrightarrow 3Cl_2$$

$$Cl + Cl_3 \longrightarrow 2Cl_2$$

Equations (1) and (2) can involve a third body, M.

It was shown that in observations where the exponential "n" of the absorbed light intensity (I_{abs}) was equal to unity, the reaction chains are believed to be terminated by adsorption of chlorine atoms and Cl_3 molecules on the walls, as in the case of ultra-violet light. Values of "n" between 1.0 and 0.5 are due to the gaseous reactions

$$2\,Cl_3 \longrightarrow 3\,Cl_2$$

$$Cl + Cl_3 \rightarrow 2\,Cl_2$$

whereas values of "n" less than 0.5 are the result of localised illumination and diffusion of chlorine atoms out of this zone into the dark space in the reaction cell.

Ritchie and Smith,[38] carrying out experiments in the oxygen-free system using a high light intensity, and Ritchie and Taylor,[5] examining the same system from the point of view, especially, of added inert gases, concluded that there is no proportional relationship between the rate of reaction and a constant power of I_{abs}, but rather that an exponential will be obtained, progressively changing as the intensity is reduced.

Considering those reactions involving Cl_3:

$$Cl + Cl_2 + M \rightarrow Cl_3 + M$$

$$2\,Cl_3 \longrightarrow 3\,Cl_2$$

$$Cl_3\ (+\ M) \longrightarrow Cl_2 + Cl\ (+\ M)$$

Where I_{abs} is the only variable, an expression was deduced of the type:

$$\gamma_{HCl} = \frac{\frac{d[HCl]}{dt}}{I_{abs}} = a\left[1 + \frac{b}{\sqrt{I_{abs}}}\right]$$

At low intensities, the reaction rate becomes proportional to I_{abs}^{n}, where "n" approaches 0.5 i.e. the γ_{HCl} tends to be inversely proportional to $I_{abs}^{\frac{1}{2}}$.

At high intensities, "n" tends to unity, and the rate of reaction becomes directly proportional to the intensity of the absorbed light. Assuming the presence of Cl_3, this can be explained by the high concentration of Cl_3 combining with itself, and hence the quantum efficiency becomes independent of the absorbed intensity.

However, although it is now generally agreed that the assumption of a Cl_3 particle facilitates the kinetics of reactions, such as that between hydrogen and chlorine, Bodenstein, who has carried out many investigations on this reaction, denies its existence and considers it an unnecessary factor in a reaction scheme.

The only case in which he refers to the possibility of a Cl_3 molecule is in a paper[39] on the photosynthesis of phosgene, when he criticises, somewhat scathingly, the inclusion by Rollefson[40] of the Cl_3 particle in his reaction scheme, pointing out that it is not essential. However, no reason is offered against the possibility of its presence.

In a review of the hydrogen-chlorine photoreaction over the last hundred years, published just before his death, Bodenstein[41] makes no reference to the possibility of the presence of Cl_3 molecules in the reaction.

A further theoretical reason for the presence of Cl_3 molecules, and their mode of formation, arose out of an investigation by Ritchie and Smith[8] into the Budde effect in chlorine.

Previously, Born and Franck[42] had deduced that a triple collison was necessary to form a homopolor diatomic molecule from two atoms. This was shown to be true in the case of bromine by Herzfeld[43] in his "dreierstoss" theory, and confirmed, inter alios by Smith, Ritchie and Ludlam.[44] i.e.

$$Br + Br + M \longrightarrow Br_2 + M$$

Ritchie and Smith[8] found that the Budde effect in chlorine could not be similarly explained. If the mechanism

$$Cl + Cl + M \longrightarrow Cl_2 + M$$

did hold, the value of Δp, the pressure change, would not be proportional to I_{abs}. This was not so.

A second mechanism was based on the reactions

$$Cl + Cl_2 \longrightarrow Cl_3$$

$$2\ Cl_3 \longrightarrow 3\ Cl_2$$

Removal of Cl and Cl_3 on the wall.

If this were so, Δp should be proportional to I_{abs} (which it is), but also inversely proportional to $S + K\,[Cl_2]$ where S is the factor representing the rate of diffusion of chlorine atoms to the wall. This was indirectly tested and found not to hold.

The third mechanism depended on the reactions

$$Cl + Cl_2 + M \rightarrow Cl_3 + M$$

$$2\ Cl_3 \rightarrow 3\ Cl_2$$

$$Cl \rightarrow \tfrac{1}{2}\ Cl_2\text{, at wall.}$$

This gives rise to the equation,

$$\Delta p = \frac{1}{R\,K\,(1 + Z)}$$

where R is a constant, K the thermal conductivity of the inert gas, and Z is a term including the $[Cl_2]$.

This was found to hold well over pressure ranges, up to 600 mms for the inert gases - nitrogen, argon, oxygen, HCl, and CO_2, acting as the third body M in triple collisions.

During these observations, an interesting pressure effect was noted, after a number of Budde effect experiments had been carried out.

When certain mixtures of chlorine and inert gas were initially illuminated, instead of a direct rise in pressure taking place, an increase to a maximum was obtained, which dropped slightly to a final steady value. Similarly, on cutting off the light, the pressure decreased to a minimum, before rising to the original value.

The maximum was attained approximately 20 seconds after the vessel was first illuminated. The minimum, on cutting off the light, took slightly longer.

Using 50 mm of chlorine, and varying amounts of the inert gases, - oxygen, nitrogen and argon, it was found that the effect was zero at low and high

(600 mm and over) pressures of the inert gas, and possessed a maximum value at 300 mm, corresponding to 0.8 of a scale division on the Bourdon gauge, i.e. .038 mm mercury pressure for the gauge used. The effect was not observed when using hydrogen chloride and carbon dioxide as inert gases.

It was shown that the effect was not attributable to a temperature change. This might be considered possible, on illumination of the vessel, before thermal conductivity equilibrium was attained, but this could not explain the analagous effect, on cutting off the light.

The effect was attributed to a species produced by illumination, the final decrease in pressure being due to its adsorption on the walls of the vessel. This adsorption continues throughout illumination.

On cutting off the light, a minimum value is reached, gradually rising to the final value, as desorption occurs.

Chlorine atoms were not considered responsible, as the effect was not observed when no added gas was present. It was suggested that Cl_3 molecules are produced by triple collisions, on adding the inert gas. At very high pressures, however, the inert gas impedes the Cl_3 molecules from reaching the walls and being adsorbed, and hence prevents the occurrence of an analagous effect. The absence of the effect in the presence of hydrogen chloride and carbon dioxide is ascribed to their own considerable powers of adsorption, thus altering the nature of the walls.

The following section gives an account of an attempted repetition of Ritchie and Smith's[8] work from this point of view.

Procedure and Results.

The apparatus used, was as described previously, but with a few slight modifications. The photometric system was not included, the manometer being considered sufficient to measure the pressures of gases involved.

Rigid temperature control of the reaction vessel was an essential throughout the measurements. This can be seen from the fact that gases at a pressure of 350 mm (a normal value) in the reaction vessel, will give rise to a pressure change of 0.01 mm for a corresponding temperature change of $\frac{1^{\circ}}{100}$C. The largest value, under the most favourable conditions, obtained by Ritchie and Smith[8] for their pressure effect, was 0.04 mm. Hence, the flow of water through the reaction vessel thermostat was maintained at as steady a rate as possible. Further, in order to check any change in temperature which may occur, a Beckmann thermometer, capable of reading to $\frac{1^{\circ}}{1000}$C was immersed in the thermostat water, and frequently read during any measurement taken. Observations were discarded, when a temperature change occurred.

In the following tables, the actual conditions under which the experiments were conducted, are recorded, along with the corresponding Budde Effects observed.

In no case, throughout the whole series of observations, was the effect, previously noted by Ritchie and Smith, satisfactorily repeated. Several times, a small pressure change (in the neighbourhood of 0.01 mm) was seen, which could have been accounted for by the special effect, but in every case, a small change in temperature in the thermostat occurred simultaneously, and, when the observation was repeated shortly afterwards under conditions of constant temperature, in no case was the change again observed.

Observation 1.

The original measurements carried out by Ritchie and Smith[8] were made using a spherical 1500 ml reaction vessel of soft glass. The only filter arrangement was a 5% solution of copper sulphate (2 cm depth, to remove heat rays) contained in a spherical 500 ml flask, which also acted as a focussing arrangement.

In the early experiments, these conditions were observed as far as possible.

Conditions:

Temperature	25°C.
Lens	Spherical bulb (500ml).
Filter	2cm. 5% $CuSO_4$ solution.
Vessel	1500ml, spherical, soft glass.
Inert gas	Nitrogen.
Sensitivity of Bourdon gauge:	0.07 mm per scale division.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	0.9
	100	1.1
	200	1.3
	300	1.9
100	0	2.1
	100	2.8
	300	3.6
200	0	3.0
	100	3.2
	200	3.5

Observation 2.

Other vessels of varying sizes and composition were now tested, in place of the 1500ml spherical bulb.

Since this effect was considered by Ritchie and Smith to be influenced by the surface - with regard to adsorption of the gas, - it was presumed that the shape and composition of the vessels might have some effect.

Conditions: As in Observation 1, except for:

(a)Vessel: 200ml, spherical, soft glass.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
25	0	0.3
	100	0.6
	200	0.8
	300	1.0
50	0	0.7
	100	1.2
	200	1.5
	300	1.7
75	0	1.0
	200	1.6

(b) Vessel 50ml, cylindrical, silica.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	0.5
	100	0.9
	200	1.2
	300	1.5
100	0	1.3
	100	1.6
	200	1.8
	300	2.1

Observation 3.

The sensitivity of the Bourdon Gauge, as used by Ritchie and Smith, was 0.048 mm per scale division. So far, the sensitivity of the gauge used throughout these experiments has been 0.07 mm per scale division.

To approach as closely as possible to the original conditions, a new, more sensitive gauge was sealed into the apparatus.

Conditions:-

Temperature	25°C.
Lens	Spherical bulb (500ml).
Filter	2cm. 5% $CuSO_4$ solution.
Vessel	1500ml, spherical, soft glass.
Inert gas	Nitrogen.

Sensitivity of Bourdon gauge: 0.046 mm per scale division.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	1.4
	200	2.8
	300	3.2
100	0	2.2
	100	3.0
	200	3.5
	300	4.3
150	0	3.0
	100	3.9
	200	4.6

Observation 4.

Due to the desirability of obtaining as rapid a thermal equilibrium as possible in the gas mixture, a special thin glass vessel was tested.

Conditions: As in observation 3, except for

Vessel: 1000ml, spherical, thin soft glass.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	1.0
	100	1.8
	200	2.3
	300	3.1
100	0	2.3
	100	2.9
	200	3.7

Observation 5.

The temperature of the gaseous mixture is considered to be an important factor in connection with the stability of any modification of chlorine produced.

Rollefson and Eyring,[35] in their original calculations from quantum-mechanical data, showed that the value of Kp, the equilibrium constant, for the reaction $Cl + Cl_2 \longrightarrow Cl_3$ would vary with temperature in fact would become greater, the lower the temperature. Since conditions are desired, in which the $[Cl_3]$ is as high as possible, a series of observations at low temperature were carried out.

The matter may also be regarded from the point of view of the inert gas, acting as the 3rd body, in a triple collision mechanism.

If Cl_3 is formed by the mechanism proposed in the hydrogen-chlorine combination, then

	Velocity Coefficient
$Cl_2 \xrightarrow{h\nu} Cl + Cl$	K_1
$Cl + Cl_2 + M \longrightarrow Cl_3 + M$	K_2
$Cl_3 + M \longrightarrow Cl_2 + Cl + M$	K_3
$Cl_3 + Cl_3 \longrightarrow 3Cl_2$	K_4
$Cl + Cl_3 \longrightarrow 2Cl_2$	K_5

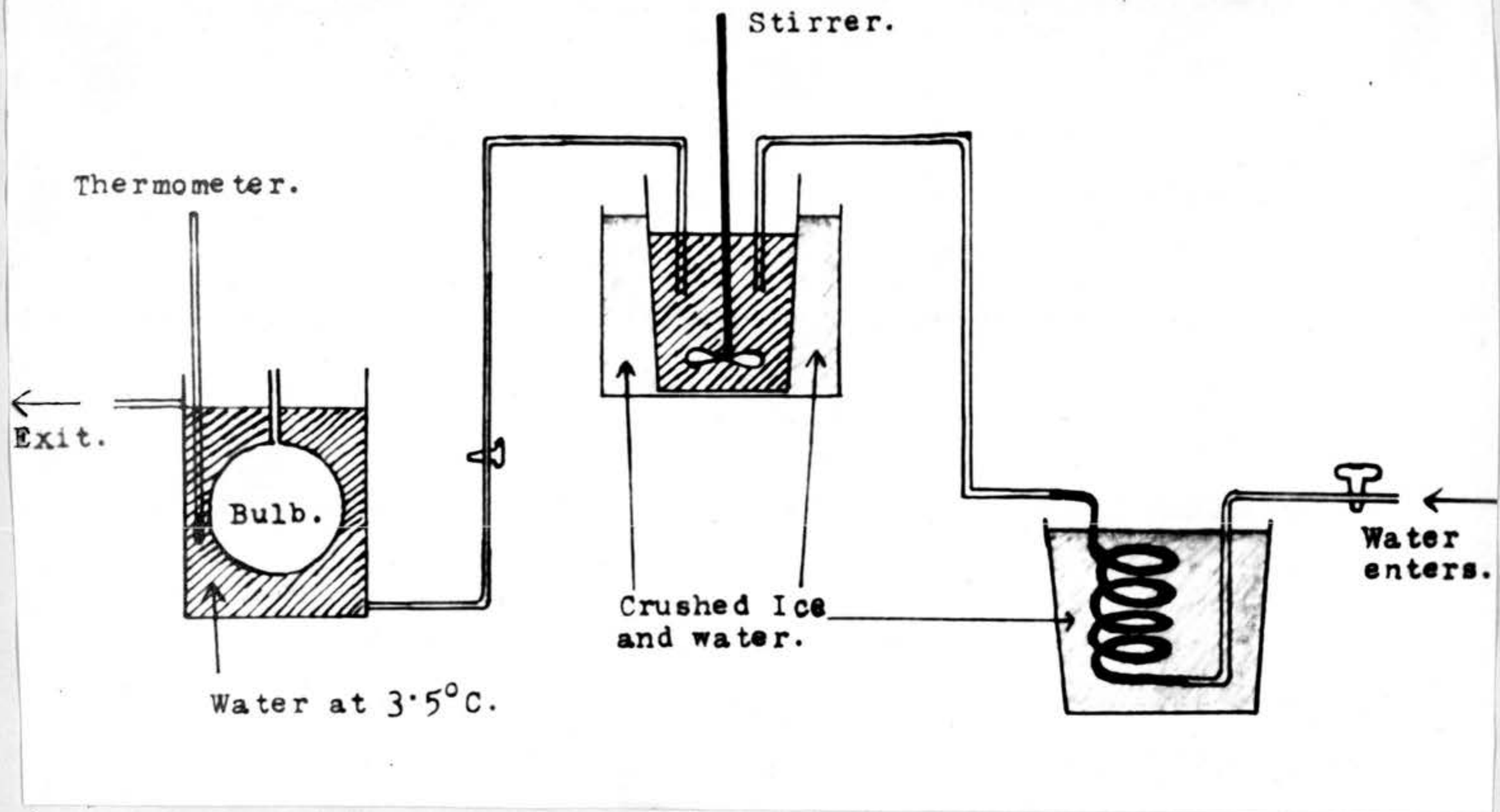
Neglecting surface actions, the concentration of $[Cl_3]$ under equilibrium conditions can be found thus:

In the photostationary state,

$$\frac{d[Cl]}{dt} = k_1 I_{abs} - k_2[Cl][Cl_2][M] + k_3[Cl_3][M] - k_5[Cl][Cl_3] = 0$$

$$\frac{d[Cl_3]}{dt} = k_2[Cl][Cl_2][M] - k_3[Cl_3][M] - k_4[Cl_3]^2 - k_5[Cl][Cl_3] = 0$$

$$\therefore k_4[Cl_3]^2 = k_1 I_{abs} - 2k_5[Cl][Cl_3]$$


Stirrer.
Thermometer.
Exit.
Bulb.
Water at 3·5°C.
Crushed Ice and water.
Water enters.

If $[Cl_3]$ attains any measureable concentration, $k_5[Cl][Cl_3]$ will be small compared with $k_4[Cl_3]^2$

Neglecting $k_5[Cl][Cl_3]$

$$[Cl_3] \doteqdot \sqrt{\frac{k_1 I_{abs}}{k_4}}$$

$\therefore [Cl_3]$ will increase as the temperature is lowered. This will probably not be a large effect, since the energy of activation of reaction 4 is probably small.

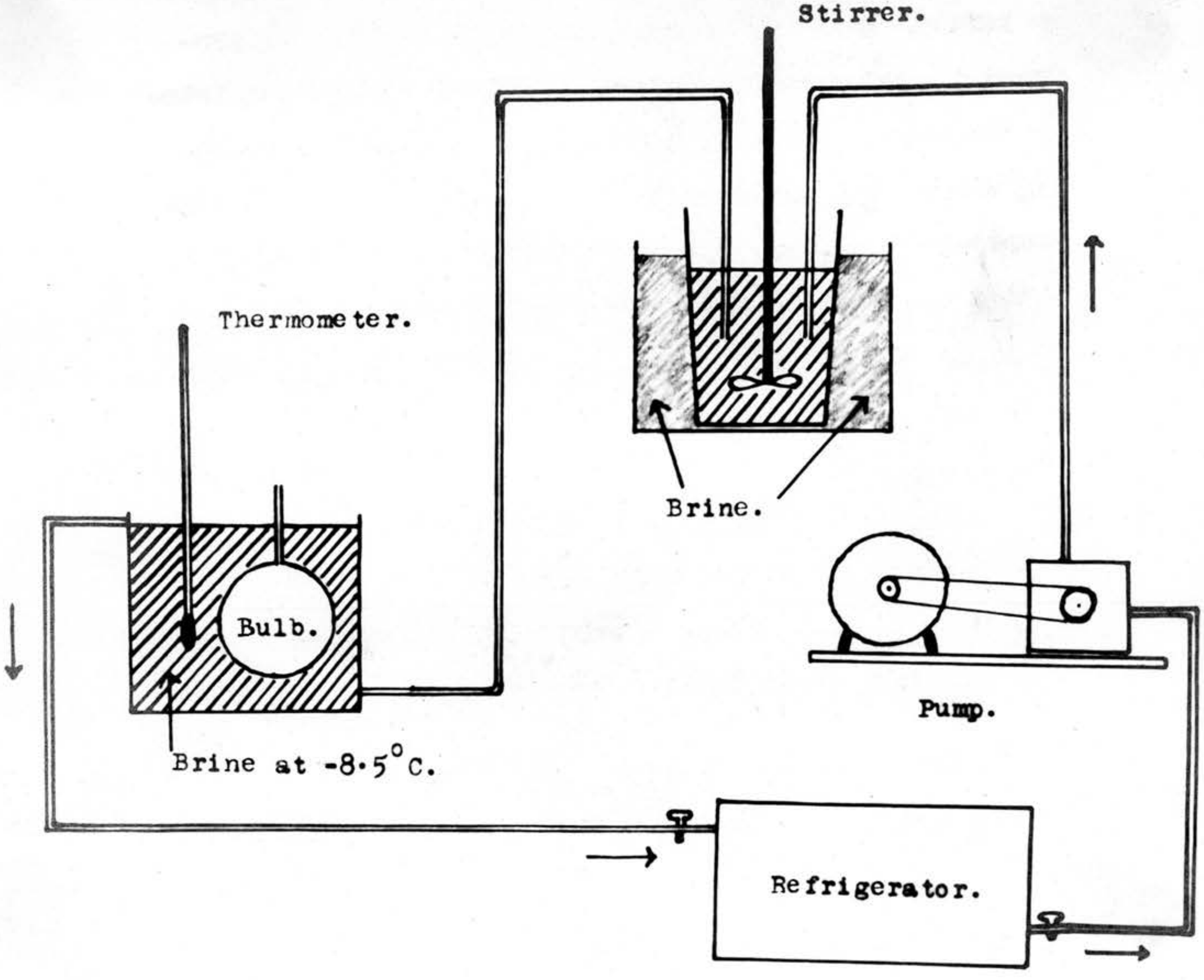
The temperatures, at which observations were now carried out, were 3.5°C and -8°C.

The experimental conditions were complicated by the importance of maintaining the temperatures at as constant a value as possible over a period of minutes.

A diagram of the apparatus, by which a constant temperature of 3.5°C was attained, is shown opposite.

Water is slowly passed through a coil immersed in a mixture of crushed ice and water. It cannot be directly led to the thermostat due to inconstancy of the temperature over a time-period. This difficulty was eliminated by first leading it to a 4-litre, thick glass vessel surrounded by an ice-water mixture. In this vessel, the water is thoroughly stirred, before passing it finally to the thermostat.

To obtain a temperature below the freezing-point of water, a strong brine solution was used as


Stirrer.
Thermometer.
Brine.
Bulb.
Pump.
Brine at -8·5°C.
Refrigerator.

the thermostat liquid. The brine could not be pumped directly from the refrigerator to the reaction vessel thermostat, due, not only to the temperature-variation as before, but also to myriads of minute bubbles produced in the pumping process, hence obscuring completely the reaction vessel from the light. An intervening vessel was employed as in the previous case. The temperature of the brine in the refrigerator reached -15°C, and in the thermostat itself, -8°C. Diagram as opposite.

5(a) Conditions:

Temperature	3.5°C.
Lens	Spherical bulb (500ml).
Filter	2cm. 5% $CuSO_4$
Vessel	1500ml, spherical, soft glass
Sensitivity of Bourdon gauge:	0.046 mm per scale division.
Inert gas	Nitrogen.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	1.4
	100	1.8
	200	2.5
	300	3.0
100	0	2.6
	100	2.9
	200	3.8
	300	4.2
200	0	4.2
	100	5.0
	200	5.5

5(b) Conditions: As in 5(a), except for

Temperature -8°C.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	1.2
	200	2.6
	300	3.2
100	0	2.2
	200	3.7
	300	4.1
200	0	3.7
	200	5.2

Observation 6.

In their original experiments, Ritchie and Smith obtained their effects with O_2 as well as N_2. Hence, cylinder oxygen, purified as previously described, was substituted for nitrogen as the inert gas.

Conditions:

Temperature	25°C.
Lens	Spherical bulb (500ml).
Filter	2cm. 5% $CuSO_4$ solution.
Vessel	1500ml, spherical, soft glass.
Sensitivity of Bourdon gauge:	0.046 mm per scale division.
Inert Gas	Oxygen.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	1.1
	100	1.9
	200	2.2
	300	3.1
100	0	2.2
	100	2.7
	200	3.4

At this stage, a much increased intensity of light was obtained by removing completely the protection round the mercury lamp. This resulted in a corresponding increase in the Budde effect by a factor of about 10.

It was expected that such an increase in the size of the Budde effect would make more evident any associated pressure change. In the original experiments of Ritchie and Smith, the special pressure change noted by them was approximately 10% of the magnitude of the Budde effect.

By using this technique, Budde effects of the order of 20-50 scale divisions were found. A corresponding temporary pressure change of 2-5 scale divisions would have been expected.

Observation 7.

The effect of variation of the surface of the reaction vessel was next examined, from two points of view.

<u>First</u>: Coating the surface of the glass vessel with a thin film of KCl. This was done by washing out the inside of the bulb with a 5% solution of KCl, ejecting all surplus liquid and drying under a vacuum.

(7a) Conditions:

Temperature	25°C.
Lens	Spherical bulb (500ml).
Filter	2cm, 5% $CuSO_4$ solution.
Vessel	1500ml, spherical, soft glass, interior coated with KCl.
Sensitivity of Bourdon gauge:	0.046 mm per scale division.
Inert gas	Nitrogen.

Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale divisions)
50	0	13.1
	100	17.8
	200	23.9
	300	30.1
100	0	22.1
	100	27.5
	200	35.9
200	0	37.2
	200	48.7

<u>Second</u>: In place of the 1500 ml spherical, soft-glass vessel used in most of the experiments, vessels of silica, of various sizes, were tested out.

(7b) <u>Conditions</u>: As in Observation 7(a) except for:

Vessels Of various sizes (1000 ml, 500 ml, 250 ml) spherical, composed of silica.

	Chlorine. (mm)	Inert Gas. (mm)	Budde Effect. (scale division)
Vessel, 1000 ml	50	0	7.9
		200	12.1
		300	15.7
	100	0	11.8
		200	16.7
Vessel, 500 ml	50	0	7.4
		200	11.3
		300	14.9
	100	0	11.5
		200	15.1
Vessel, 250 ml	50	0	3.4
		200	6.5
		300	8.9
	100	0	7.9
		200	12.0

<u>Observation 8</u>.

As no direct evidence for the effect obtained by Ritchie and Smith could be obtained, indirect evidence was sought by examining the rates of cooling of gas mixtures, when illumination was cut off.

By applying Newton's law of cooling to the resultant data, it was intended to find whether there was a good agreement experimentally, and if not, whether any discrepancies could be attributed to an unusual form of chlorine.

The same 1000 ml vessel was again used as in the last observations, and two gas mixtures examined.[*]

t	time in seconds.
Δp	the pressure change.
ΔT	the corresponding temperature change.
T_{av}	the average relative temperature over the time interval.
T	the final relative temperature.

Gas Mixture: 50 mm chlorine + 300 mm oxygen.

Time t secs.	Pointer Reading Scale divs.	$\frac{d\Delta p}{dt} \propto \frac{d\Delta T}{dt}$	$T_{av} - T$
0	40.0		
4	28.5	2.88	11.2
8	25.1	0.85	3.7
12	24.0	0.28	1.5
16	23.3	0.18	0.6
20	23.1	0.05	0.1
30	23.1	-	-
40	23.1	-	-
60	23.1	-	-

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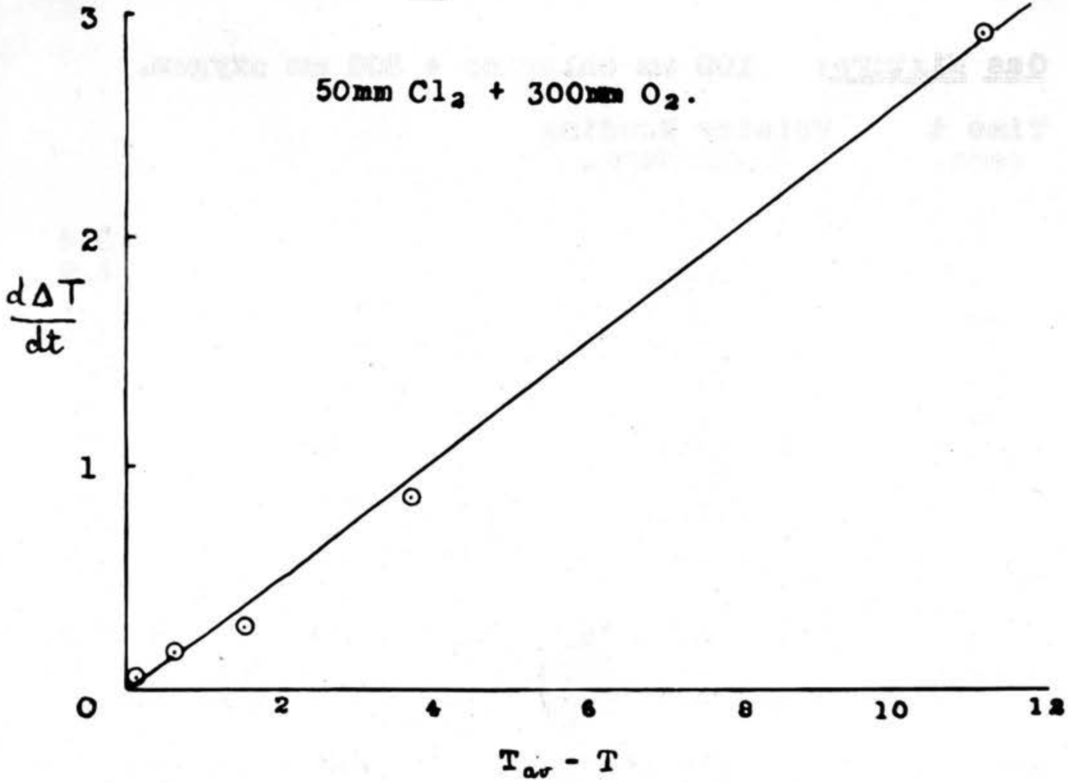
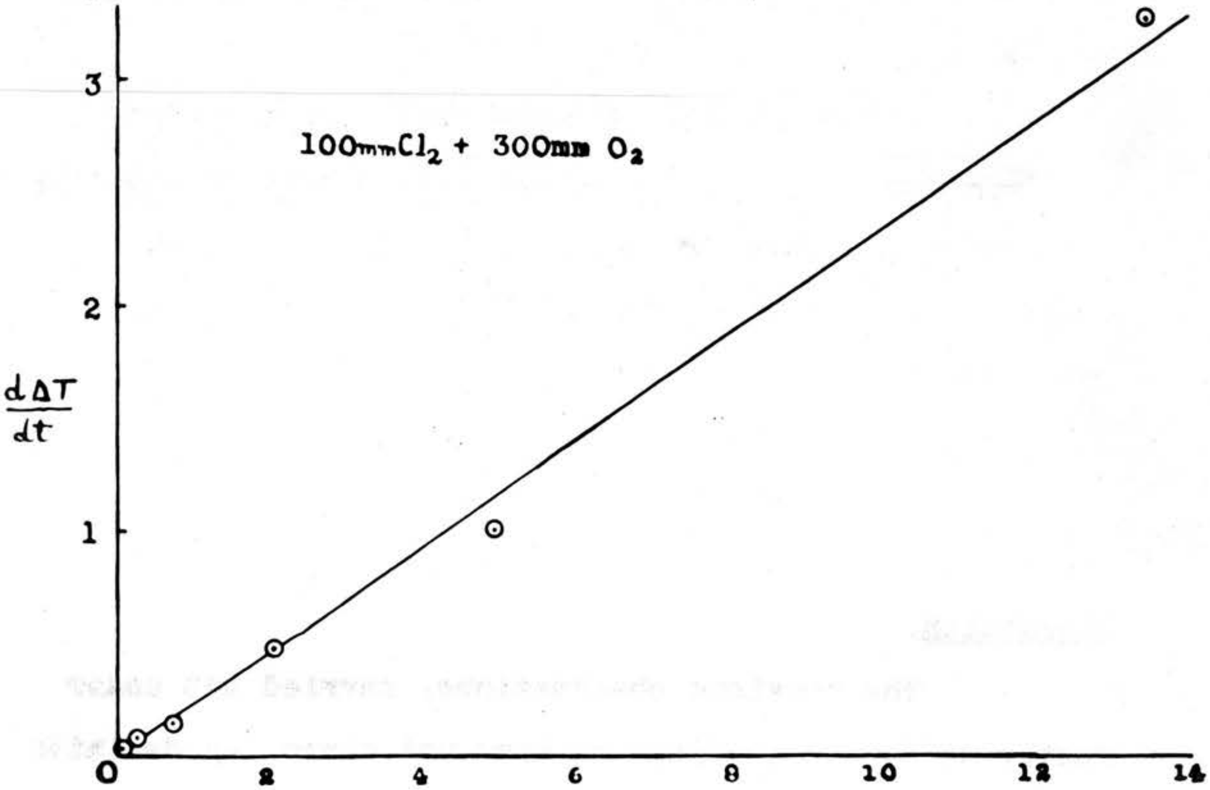
[*] I am indebted to Mr. W. Lonie, B.Sc., for his assistance during these observations.

Graph: $\frac{d\Delta T}{dt}$ against $T_{av} - T$





Gas Mixture: 100 mm chlorine + 300 mm oxygen.

Time t secs.	Pointer Reading Scale divs.	$\frac{d\Delta p}{dt} \propto \frac{d\Delta T}{dt}$	$T_{av} - T$
0	70.0		
4	57.0	3.25	13.4
8	53.0	1.00	4.9
12	51.1	0.48	2.0
16	50.5	0.15	0.7
20	50.2	0.075	0.25
24	50.1	0.025	0.05
30	50.1	-	-
40	50.1	-	-
60	50.1	-	-

By Newton's law, the rate of loss of heat, $\frac{d\Delta T}{dt}$, from the body at any instant is directly proportional to the excess of the temperature of the body over the surroundings, if other conditions remain constant.

Hence, if the law holds here, on plotting $\frac{d\Delta T}{dt}$ against $T_{av} - T$, a straight line should be obtained. The graphs opposite show this to be very nearly the case, - certainly no definite trend otherwise could be asserted.

Discussion.

The previous observations, carried out under vastly different conditions, have not given any definite evidence of unusual phenomena occurring on ceasing to illuminate gas mixtures of chlorine and inert gases.

It remains to attempt to explain how the previous observations could have been found. Three possible explanations can be suggested.

1. The effect might come about due to an expansion of the glass, after illumination has been commenced. The previous pressure change, due to the Budde effect raising the temperature of the gas, having taken place completely, the glass itself might then expand, and cause a decrease in volume to occur, registered as a pressure change on the Bourdon gauge.

   However if the expected magnitude of the effect is calculated from Ritchie and Smith's results, it is found that the temperature of the gas would increase by 0.245°C for a corresponding Budde effect of 6 scale divisions (= 0.288 mm pressure change), and assuming normal values of the temperature coefficient of glass, this would result in a pressure change of at most 0.05 of a scale division, compared with 0.8 obtained experimentally.

   It is concluded that this effect alone cannot account for the observation.

2. While the previous effect might take place to a very small extent when illumination is commenced,

it cannot take place, even qualitatively, when illumination is cut off, if the whole volume of gas is surrounded by water at constant temperature.

Under the latter conditions, the assumption would have to be made that, when illumination ceases, the gas cools before the vessel has had time to assume the temperature of the thermostat water. This cannot occur if the water entirely surrounds the vessel, otherwise we would have heat passing from a cold body (gas) to a hot body (the vessel wall) and thence to the water.

The explanation would only hold, if the gas is cooled rapidly to a lower temperature than that of the vessel walls, by, for example, a not entirely covered vessel.

3. When the gas expands, on illumination, some might be driven from the vessel into the connecting tubes, and then subsequently cool to room temperature, a decrease in pressure thereby taking place.

For a vessel capacity of 1500 ml, and a difference in temperature of the air and thermostat water of 10°C, such an effect would produce a pressure change of about 0.2 of a scale division, for the previous conditions, defined by Ritchie and Smith. This is one-quarter of the effect originally observed, but might partially account for the phenomenon.

No satisfactory explanation of the effect found by Ritchie and Smith[8], has thus been devised.

Part II. THE PRIMARY PHOTO- AND THERMAL REACTION BETWEEN TOLUENE AND CHLORINE IN THE GAS PHASE.

Introduction.

While it has been possible in the past to attribute certain experimental phenomena, e.g. Budde effect observations, to a chlorine molecule of three atoms, the theoretical evidence arising from attempts to elucidate the kinetics of the hydrogen-chlorine photo-reaction gives much more convincing sanction for its existence.

Little investigation has been made of the photo-reaction between toluene and chlorine in the gas phase. The corresponding liquid phase reaction has been examined to some extent, but due to the obvious complexity of such a system, no comprehensive mechanisms have been suggested. It was hence decided to look into this gas reaction further, with the ultimate object of finding other evidence for or against the existence of new forms of chlorine.

A very early investigation by Luther and Goldberg[45] on photo-reactions of chlorine with various organic substances in the gaseous state, showed, as expected, that oxygen exerts a strong retarding action. In particular the reaction with toluene is mentioned.

Other examinations of this photo-reaction in the gas phase are described in two papers on the industrial production of chloro-derivatives of toluene. Gibbs and Geiger[46] describe a process whereby toluene, mixed with varying proportions of chlorine, produce either benzyl chloride, benzal chloride or benzotrichloride, almost completely, on irradiation with U-V light. A similar type of process for the production of benzyl chloride was described by Ellis[47]. In this case, the reaction is carried out at a temperature of 150°C, and under the influence of mercury light.

The reaction of chlorine with liquid toluene is described by Book and Eggert[48]. When toluene was chlorinated just below its boiling-point, they found that benzyl chloride was almost the only product, no matter whether the reaction was carried out in light or in darkness, provided that no chlorine carriers were present. At a temperature of - 80°C, whereas the dark reaction was almost entirely suppressed, a photoreaction could be brought about by suitable illumination. The quantum efficiency of this reaction was about 25 molecules per quantum of light absorbed, and the products were chlorotoluene and benzyl chloride, along with HCl. Under these conditions, a trace of iodine or phosphorus pentachloride accelerated the reaction.

However, both these statements were refuted by Bergel.[49] In a series of reactions in the presence and absence of sun-light, he found that the reaction was materially accelerated, in the latter case. He also found no evidence for the belief that phosphorus pentachloride catalyses the chlorination.

Carrying out analogous, but more comprehensive, observations to those of Book and Eggert,[48] it was shown by Olivier[50] that the products formed and their proportions depended on the type and intensity of light used. Knowing values of the velocity constants of the possible reactions taking place, conclusions were drawn as to the proportions of each product formed, Since the reactions producing both benzo-trichloride and benzyl chloride possess high velocity constants, an initial rapid rate of reaction would suggest their formation. This was found experimentally to be the case, on illumination with each light source. In the second stage of the reaction, the rate falls, but not far enough to suggest that only compounds of the type $Cl.C_6H_4.CH_3$ and $Cl.C_6H_4.CH_2Cl$ are formed. He suggests derivatives of cyclo-chloro-hexane as possible products of the reaction.

Whereas the chlorine has initially been introduced in the gaseous state in all the previous examinations, a series of experiments in which reaction occurs between liquid chlorine and liquid toluene is described by Kharasch and Berkman.[51] At a temperature of 0°C and in the total absence of air, it was found that both in the dark and on illumination, out of the 99% of chlorine which reacted, 54% was used by substitution in the side-chain, and 45% by addition to the nucleus. While this result was obtained after 20 hours in complete darkness, the same result was found after 30 seconds illumination. Under these latter conditions, the presence of oxygen appeared to retard the reaction only slightly. This is in contradiction to the results of other investigations, and is probably explained by the fact that the presence of oxygen will not be so effective in the entirely liquid-phase reaction.

A short investigation was carried out by Taylor[52] into the gas-phase reaction, employing a similar type of apparatus to that used in the present research. The reaction was carried out in a vessel of about 1 litre in volume, illuminated by 406 mu light. The residual chlorine and HCl was determined volumetrically.

It was found that the reaction in the absence of oxygen was very rapid, the quantum efficiency being in the region of 10^3 or 10^4 molecules per quantum, indicating a chain mechanism present. The addition of even 1 mm of oxygen cut down the reaction rate considerably.

The presence of a thermal reaction was also noted at the temperature of the observations, but was observed to be inconsiderable compared with the photo-reaction.

In the present investigation, it was decided first to determine to what extent oxygen retards the reaction, as observed previously. During this examination, the presence of the thermal reaction - also retarded by oxygen - became obvious, and a measure of its magnitude was carried out.

This thermal reaction, in the absence of oxygen, was next examined quantitatively. Finally, a value was obtained of the quantum efficiency in the oxygen-free system.

Experimental.

The main distinction in the experimental procedure using toluene, in place of hydrogen, was that the toluene must be the first substance to be introduced into the reaction vessel, due to its low vapour pressure at the temperature of the observation.

After allowing the toluene to liquify in the reservoir, and drawing off the vapour several times, it was found convenient to surround the reservoir with water at a temperature, about 10° above that of the room. The reaction vessel was "washed out" several times with the toluene vapour, and finally exactly 15 mm were introduced. Depending on the room temperature, it was occasionally possible to obtain a few mm higher pressure of vapour, but as this maximum varied from day to day, the figure of 15 mm was taken each time.

The gradual solution of the toluene vapour in the tap-grease has been referred to previously in the experimental procedure.

PHOTO- AND THERMAL REACTIONS IN THE PRESENCE OF OXYGEN.

Although the strong inhibiting effect of oxygen was noted by Luther and Goldberg[45] and by Taylor,[52] no systematic quantitative examination has so far been carried out.

The magnitude of the photo-reaction in the presence of varying pressures of oxygen was examined with these objects: to find out if it obeyed the analogous relationship to the hydrogen-chlorine case, in which the product of oxygen concentration and quantum efficiency attains a maximum value at high pressures of oxygen; and also, to decide, for future reference, what pressure of oxygen must be added to the chlorine-toluene gas mixture in order to "kill" the reaction sufficiently to allow the chlorine concentration to be determined photometrically.

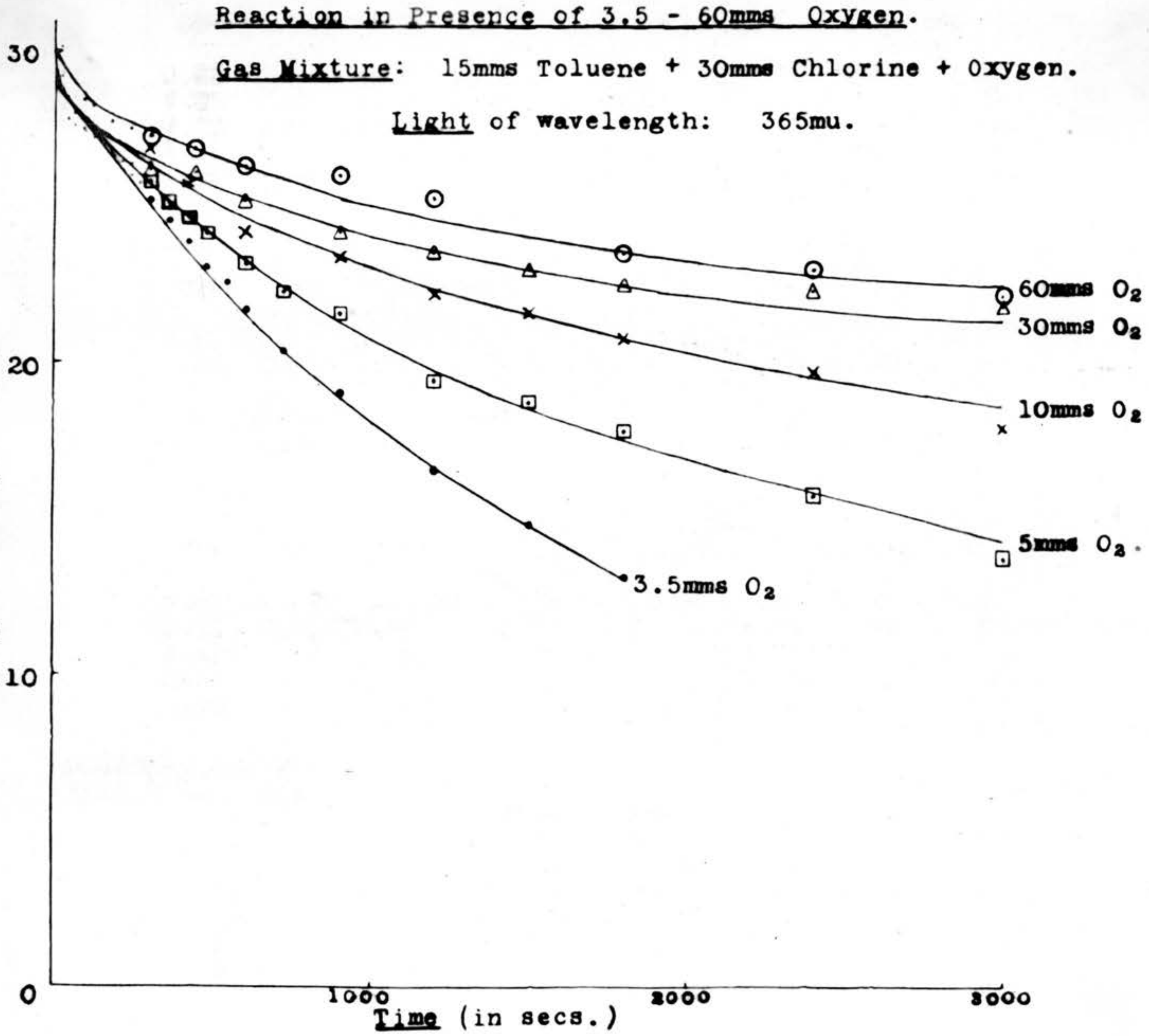
Due to the comparative slowness of the photo-observations, with oxygen present, their progress was followed using the "graphical" method. Briefly, a value of I_o was observed with the reaction vessel empty, the toluene introduced, followed by the oxygen, and then the chlorine - in that order to suppress the oxygen-free thermal reaction, referred to later, - and illumination commenced, taking galvanometer readings (and hence I) at various time intervals. Finally, the gases were evacuated, and I_0 again determined. If I had changed to a small extent from its initial value, the assumption was made that the change occurred linearly with time, and so values of $\log_{10}\frac{I_0}{I}$ and corresponding chlorine concentrations were obtained.

In observations of the photo-reaction in the presence of oxygen pressures between 3.5 and 60 mm, light of wavelength 365 mu was used. With pressures of oxygen greater than 60 mm, the reaction became too slow for accurate measurement using 365 mu light, and hence unfiltered light - except for the usual filter of 5% copper sulphate solution - was employed. The observation in the presence of 60 mm oxygen was examined with both types of light, and acted as a connecting link between the reaction at low and high pressures of oxygen in the subsequent quantum efficiency calculations.

The presence of a thermal reaction between toluene and chlorine was suspected, and the corresponding dark reaction in the presence of oxygen was examined. The procedure followed similar lines to that described in the subsequent section. In this case, the "graphical" method of measurement cannot, of course, be used, and so one value was taken in each case, 20 minutes after adding the reactants. This value is given at the end of each of the following tables, for the corresponding oxygen pressure.

In the final calculations, the assumption was made that, in the observations in the presence of light, the rate of the reaction could be regarded as composed of the sum of the thermal and photo-reactions.

The assumption was also made that the quantum efficiency of the reaction in the presence of 60 mm of oxygen could be regarded, at a first approximation, as the same using both 365 mu and unfiltered mercury light. Thus, the quantum efficiencies in mixtures with high pressures of oxygen were calculated and related to those illuminated with 365 mu light.



Reaction in Presence of 3.5 - 60mms Oxygen.

Gas Mixture: 15mms Toluene + 30mms Chlorine + Oxygen.

Light of wavelength: 365mu.

Oxygen Pressures: 3.5 - 60 mm. λ of light: 365 mu.

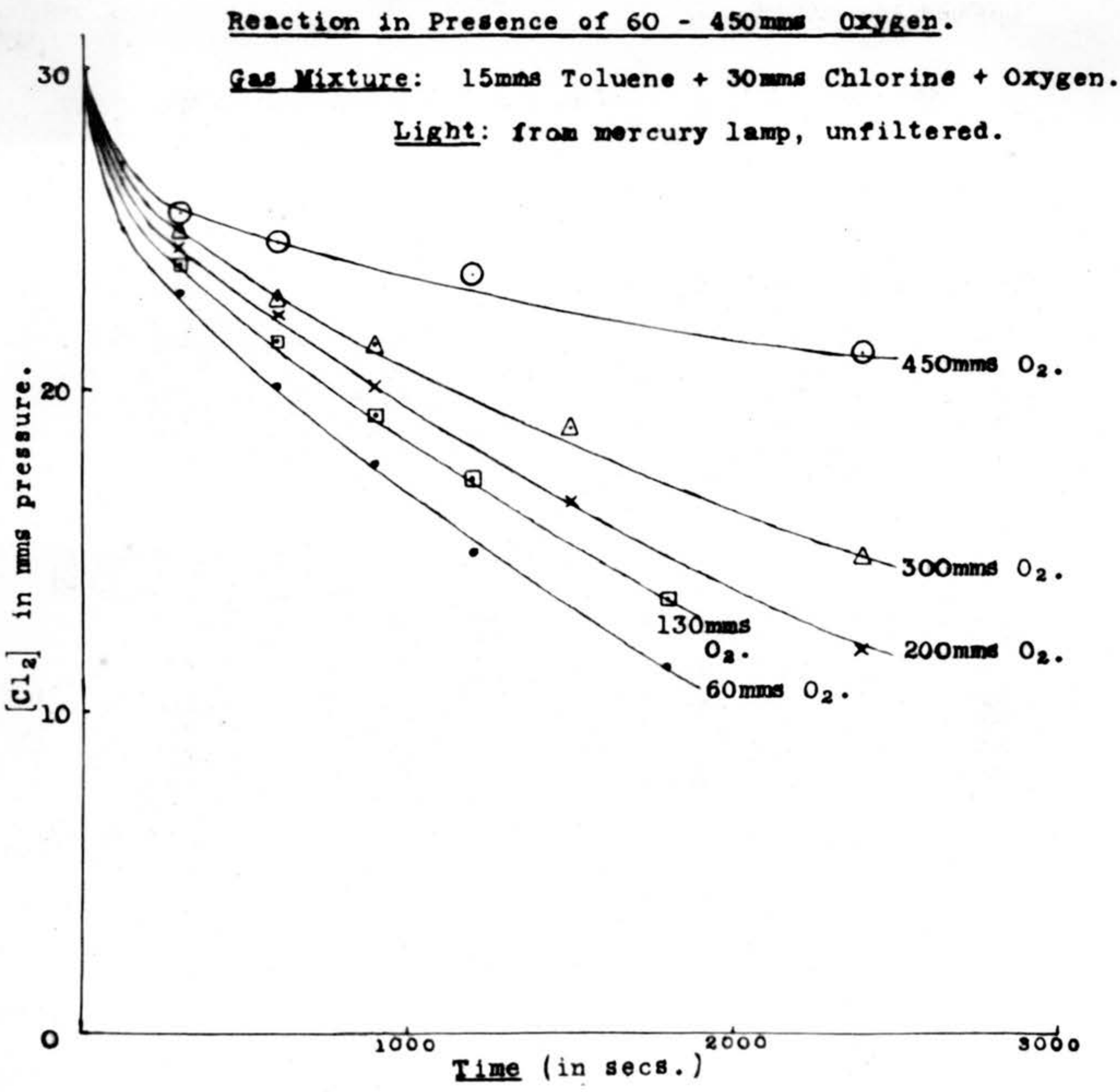
Photo-reaction

$[O_2]$ mm.	I_0 cm.	Time secs. →	0	20	40	60
3.5	37.7-37.5	$[Cl_2]$ mm.	29.9	29.5	28.5	28.0
5	41.1-40.4		29.8	29.4	29.0	28.7
10	41.6-41.2		30.1	29.5	28.9	28.7
30	39.5-38.9		29.7	29.2	27.8	27.6
60	38.2-37.6		30.3	30.1	28.5	28.5

$[O_2]$	secs. →	90	120	150	180	210	240	270
3.5	$[Cl_2]$ mm.	27.4	27.3	27.0	26.6	26.4	26.0	25.8
5		28.3	27.5	27.3	27.0	26.7	26.5	26.3
10		28.4	28.2	28.1	27.8	27.6	27.4	-
30		27.5	27.2	27.1	26.9	-	26.4	-
60		28.4	28.2	-	27.7	-	27.5	-

$[O_2]$	secs. →	300	360	420	480	600	720	900
3.5	$[Cl_2]$ mm.	25.3	24.6	23.9	23.1	21.7	20.4	19.0
5		25.8	25.1	24.7	24.2	23.2	22,3	21.6
10		27.0	-	25.9	-	24.2	-	23.4
30		26.2	-	26.1	-	25.2	-	24.2
60		27.3	-	26.9	-	26.3	-	26.0

$[O_2]$	secs. →	1200	1500	1800	2400	3000	Thermal reaction Time - 1200 secs. $[Cl_2]$
3.5	$[Cl_2]$ mm.	16.5	14.8	13.1	-	-	21.1
5		19.4	18.7	17.8	15.7	13.7	23.3
10		22.2	21.6	20.8	19.7	17.9	24.9
30		23.5	23.0	22.5	22.3	21.8	25.3
60		25.3	-	23.5	23.0	22.1	26.6



Reaction in Presence of 60 - 450mms Oxygen.

Gas Mixture: 15mms Toluene + 30mms Chlorine + Oxygen.

Light: from mercury lamp, unfiltered.

Oxygen Pressures:

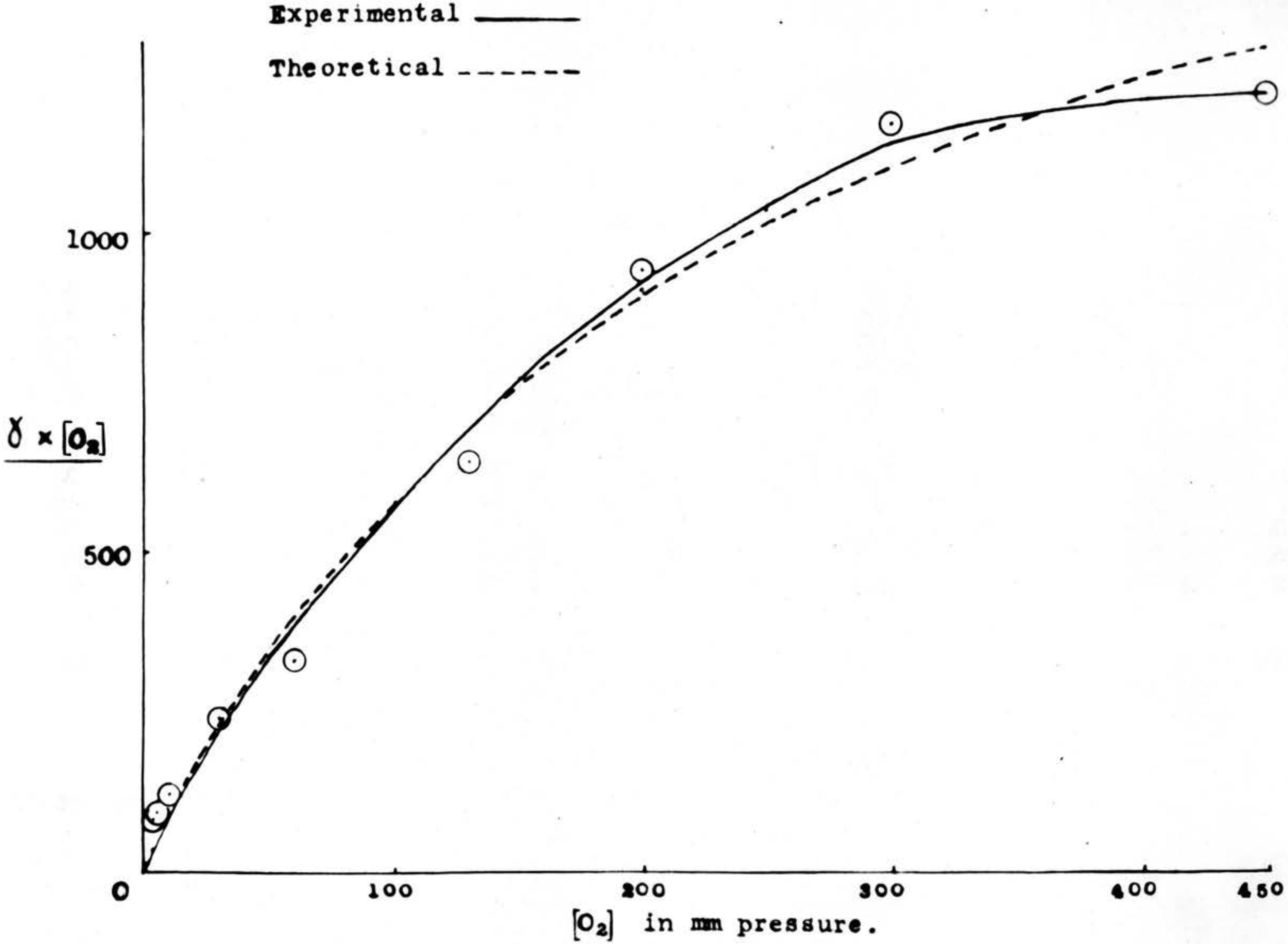
60 - 450 mm. Light - Unfiltered mercury.

$[O_2]$ mm.	I_0 cm.	Time secs.	0	120	300	600
60	33.6	$[Cl_2]$ mm.	30.0	25.0	23.0	20.1
130	33.3		30.4	26.5	23.9	21.5
200	32.6-32.8		30.1	26.6	24.5	22.5
300	34.5-34.2		30.0	26,9	25.0	22.8
450	33.8-32.8		30.4	27.0	25.5	24.6

Thermal reaction
Time - 1200 secs.

$[O_2]$	secs.	900	1200	1500	1800	2400	$[Cl_2]$
60	$[Cl_2]$ mm.	17.7	14.9	-	11.4	-	26.5
130		19.2	17.2	-	13.5	-	28,2
200		20.1	-	16.5	-	11.9	28.8
300		21.4	-	18.8	-	14.8	29.4
450		-	23.6	-	-	21.1	30.0

Graph: $\gamma \times [O_2]$ against $[O_2]$.



Quantum Efficiencies:

[Toluene] mm.	$[O_2]$ mm.	Initial $[Cl_2]$ mm.	Final $[Cl_2]$ mm. (total)	Final $[Cl_2]$ mm. (thermal)	Δ Cl_2 (photo) mm.	Time secs.	Average $[Cl_2]$ mm.	I_{ab} cm.	Relative $\gamma_{Cl_2} \times 10^{-4}$	γ_{Cl_2} Mols./$h\nu$	$\therefore \gamma_{Cl_2} \times [O_2]$
15.1	3.5	29.9	16.5	21.1	4.6	1200	23.2	7.7	4.98	22.9	80.2
15.0	5	29.8	19.4	23.3	3.9	1200	24.6	8.2	3.96	18.2	91
15.2	10	30.1	22.2	24.9	2.7	1200	26.2	8.6	2.62	12.0	120
14.9	30	29.7	23.5	25.3	1.8	1200	26.6	8.7	1.72	7.9	237
15.1	60	30.3	25.3	26.6	1.3	1200	27.8	8.9	1.22	5.5	330
15.2	60	30.0	14.9	26.6	11.7	1200	22.5	7.5	13.0	5.5	330
15.0	130	30.4	17.2	28.2	11.0	1200	23.8	7.9	11.6	4.9	637
15.2	200	30.1	18.2	28.8	10.6	1200	24.2	8.0	11.0	4.7	940
14.8	300	30.0	20.3	29.4	9.1	1200	25.2	8.2	9.25	3.9	1170
15.0	450	30.4	23.6	30.4	6.8	1200	27.0	8.8	6.44	2.7	1215

When the product $\gamma \times [O_2]$ is plotted against $[O_2]$ a graph is obtained possessing a similar shape to the corresponding graph for the oxygen-rich hydrogen-chlorine reaction, as found by Norrish and Ritchie.[3]

In the present case, with [Toluene] = 15 mm, $[Cl_2]$ = 30 mm, and at high oxygen concentration - above 300 mm - the quantum efficiency becomes inversely proportional to the $[O_2]$. In the case of the hydrogen-chlorine reaction, under the experimental conditions described by Norrish and Ritchie[3] ($[H_2]$ = 44 mm, $[Cl_2]$ = 44 mm) this relationship $\gamma \propto \frac{1}{[O_2]}$ occurred with oxygen concentrations of 10 mm and over.

Since the final product of the hydrogen-chlorine reaction is known, an expression relating the quantum efficiency to the oxygen concentration can be deduced for oxygen-rich mixtures. Such a relationship was found by the above authors, and simplified to an equation of the type:

$$\gamma = \frac{a}{b + [O_2]}$$

where "a" and "b" are constants, referring to the concentrations of the various substances present in the vessel.

Taking various points on the graph opposite, values of "a" and "b" can be found for the chlorine-toluene reaction.

Hence, taking mean values of "a" and "b" over the entire range, the corresponding values of $\gamma \times [O_2]$ can be found. On comparing these calculated values with the previous experimental values, a good agreement is observed.

The previous equation becomes:

$$\gamma \times [O_2] = \frac{a\,[O_2]}{b + [O_2]}$$

$[O_2]$ mm.	$\gamma \times [O_2]$ from graph	a	b	$\gamma \times [O_2]$ calculated
50	340			348
100	580	1970	240	581
150	770	2090	258	761
200	910	2060	253	901
250	1030	2090	258	1013
300	1130	2110	260	1104
350	1180	2010	245	1180
400	1205	1890	228	1243
450	1215	1820	218	1298

Mean value of a - 2005.
Mean value of b - 245.

Conclusions:

1. Comparing the values of the quantum efficiencies obtained here, with these in the oxygen-free state (in a later section) it is found that, in agreement with other investigators,[45, 52] oxygen exerts a powerful inhibiting action.

A hitherto unrecorded observation is that the thermal reaction, with oxygen present, plays an important part in the total rate of reaction at 25°C, under the experimental conditions of this investigation.

2. Also, it is found that the rate becomes inversely proportional to the oxygen concentration at high values of the oxygen concentration, obeying an analogous relationship to the case of the hydrogen-chlorine reaction. $\gamma_{Cl_2} = \frac{2005}{245 + [O_2]_{mm.}}$

3. The addition of 300 mm of oxygen is considered to be ample to "kill" the reaction in the oxygen-free state, for sufficient time to allow the concentration of residual chlorine to be determined photometrically, using 365 mu light.

THERMAL REACTION IN THE OXYGEN-FREE SYSTEM.

The presence of a vapour-phase thermal reaction between toluene and chlorine has been investigated at temperatures of 250°C and upwards by Mason et alia[53], using a flow system. They found that the reaction proceeds smoothly and rapidly to give side-chain chlorination products - chiefly benzyl and benzal chlorides. However, in the presence of chlorine carriers, such as traces of iodine, ferric chloride, and aluminium chloride, nuclear substitution also occurs.

Before examining the photo-reaction in the oxygen-free state, it was thus necessary to find to what extent a corresponding thermal reaction occurs at the temperature of the subsequent observations, i.e. 25°C.

The reaction vessel was carefully screened from any light, before entering the 15 mm toluene and 30 mm chlorine. Thermal reaction proceeded, and after various time intervals, 300 mm of oxygen were added, and the chlorine concentration determined in the usual way. During the progress of the thermal reaction itself, the Bourdon gauge pointer remained quite steady throughout, only a small decrease (about one mm) in pressure occurring, which could be explained by slight solution of the toluene in the tap grease. Also, after a dozen such observations, the reaction vessel showed no evidence of any deposit of tarry material (see case of photo-reaction).

Early observations indicated the presence of a thermal reaction, but not to a great extent. Later, however, when the effect was examined in detail, it was found to be of a considerable size. This discrepancy between the two observations (taken several weeks apart), suggests that the nature of the surface may be a factor to be considered.

Observations in each case were taken using 30 mm pressure of chlorine, with toluene pressures of 15 mm, 10 mm, and 5 mm.

<u>Reaction Mixture</u> I. 15 mm toluene + 30 mm chlorine.

Time of Thermal Reaction (mins.)	Final $[Cl_2]$ mm.	ΔCl_2
$\frac{1}{3}$	24.1	
	25.7	
	24.4	
1	24.1	
2	23.6	
3	21.6	
5	20.6	
10	18.7	
15	18.1	
	16.4	
25	17.4	12.6
	16.6	13.4

<u>Reaction Mixture</u> II. 10 mm toluene + 30 mm chlorine.

Time of Thermal Reaction (mins.)	Final $[Cl_2]$ mm.	ΔCl_2
5	25.1	
10	23.5	
20	22.0	8.0
	21.7	8.3

<u>Reaction Mixture</u> III. 5 mm toluene + 30 mm chlorine

Time of Thermal Reaction (mins.)	Final $[Cl_2]$ mm.	$\bar{\Delta}Cl_2$
5	27.6	
10	26.8	
20	(26.0	4.0
	(26.2	3.8

Using the above data, the graph of $[Cl_2]$ against time was plotted, and a curve drawn as evenly as possible through the various points. Hence, values of the rate of change of $[Cl_2]$ with time were obtained from tangents at various time intervals.

If the assumption is made - and justification will be given for it later, - that, in the absence of light, the principal reaction is:

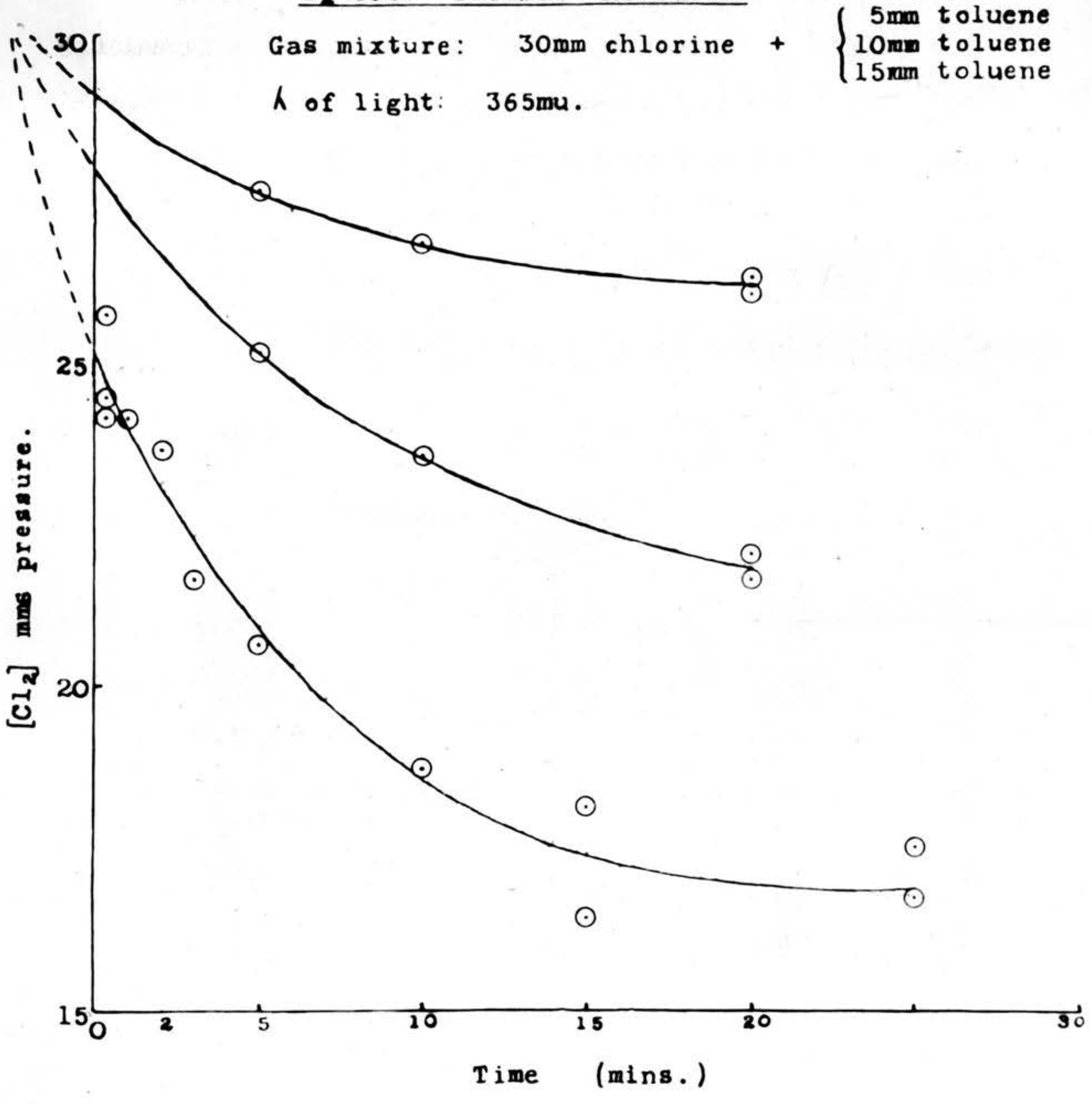
Toluene + Chlorine → Benzyl Chloride + Hydrogen Chloride

then the corresponding concentration of toluene can be immediately obtained at various time intervals.

Calculation showed that the rate of decrease of $[Cl_2]$ could be expressed by a 2nd order equation:

$$\text{Rate of decrease of } [Cl_2] \text{ with Time} = -\frac{d[Cl_2]}{dt} = k\,[Cl_2][\text{Toluene}]$$

With the rate in mm per minute and the gas concentrations in mm, values of "k" thus obtained all lay between 0.0045 and 0.0055 in the case of the three reaction mixtures.



O_2-free Thermal Reaction.

Gas mixture: 30mm chlorine + 5mm toluene / 10mm toluene / 15mm toluene

λ of light: 365mu.

Another curve was drawn, using values of $-\frac{d[Cl_2]}{dt}$ derived by substituting various chlorine and toluene concentrations, along with a constant value of K = 0.0050. As can be seen, reasonable correspondence is obtained between the deduced curve and the experimental points, between the time limits ⅓ - 25 minutes with Reaction Mixture I, and 5 - 20 minutes in the case of Reaction Mixtures II and III.

Reaction Mixture I.

t Time. (mins.)	$[Cl_2]$ mm. from graph.	[Toluene] mm.	k	Rate mm./min.
	24.1	9.1	0.0050	
⅓	25.7	10.7		
	24.4	9.4		
(average)	24.7	9.7		1.20
1	24.1	9.1		1.10
2	23.1	8.1		0.94
3	22.3	7.3		0.815
4	21.6	6.6		0.71
5	20.9	5.9		0.615
6	20.3	5.3		0.54
7	19.8	4.8		0.475
8	19.3	4.3		0.415
9	18.9	3.9		0.37
10	18.5	3.5		0.325
11	18.2	3.2		0.29
14	17.6	2.6		0.23
15	17.4	2.4		0.21
16	17.2	2.2	↓	0.19

Reaction Mixture II.

t. Time (mins.)	$[Cl_2]$ mm. from graph.	[Toluene] mm.	k	Rate mm./min.
4	25.7	5.7	0.0050	0.73
5	25.1	5.1	↓	0.64
6	24.5	4.5		0.55
9	23.9	3.9		0.47
10	23.5	3.5		0.41
11	23.1	3.1		0.36

Reaction Mixture III.

t. Time (mins.)	$[Cl_2]$ mm. from graph.	[Toluene] mm.	k	Rate mm./min.
4	28.0	3.0	0.0050	0.42
5	27.6	2.6	↓	0.36
6	27.3	2.3		0.31
9	26.8	1.8		0.24
10	26.6	1.6		0.21
11	26.4	1.4		0.18.

With reaction mixture I, it is seen that a much more rapid rate of reaction occurs within the first 20 seconds. An explanation can be given for this. After the toluene has been added to the reaction vessel, the chlorine is next introduced. When it first enters the vessel, it can be assumed that thermal reaction starts immediately. Gradually more chlorine is added, until 30 mm is registered on the manometer. The whole process of introducing the chlorine in this way takes a finite time, - about 80 seconds, varying, however, in each observation. The chlorine concentration is also simultaneously increasing from zero to 30 mm.

Although it is not feasible to regard the reaction as having begun until the chlorine is completely introduced, in actual fact, reaction has been proceeding at a gradually increasing rate since the chlorine first entered the vessel.

Hence, at the beginning of the reaction, the actual value of the time of reaction "t" is considerably larger than that measured. As "t" increases, this factor becomes of less importance, until at high values of "t", it can be neglected, without appreciable error.

By assuming this value of $K = 0.005$, a value of the rate of thermal reaction at zero time can be found, for reaction mixture I, thus:-

At $t = 0$ $[\text{Toluene}] = 15.0$ mm.

$[\text{Chlorine}] = 30.0$ mm.

Rate of reaction = $0.005 \times 15.0 \times 30.0$

= $\underline{2.25 \text{ mm per minute.}}$

Similar graphs were plotted at 2 time intervals, in the case of reaction mixtures II and III. Due to the smaller changes in chlorine concentration compared with reaction mixture I, after equal time intervals, further deductions as to the rates at the beginning of the observation, were not made.

Finally, an interesting point was noted about the extent to which the reaction proceeds in all three instances.

After 25 minutes in the case of reaction mixture I, and after 20 minutes with mixtures II and III, reaction virtually ceases, the amounts of chlorine having reacted, being:-

		Average $[Cl_2]$ reacting	Original [Toluene]
Reaction Mixture	I	13.0	15.0
	II	8.2	10.0
	III	3.9	5.0

It would hence appear that some simple quantitative relationship exists between the amounts of chlorine reacting, and the initial amount of toluene present.

If it is assumed that the only reaction which takes place quantitatively during the thermal reaction, is:

$$C_6H_5.CH_3 + Cl_2 \rightarrow C_6H_5.CH_2Cl + HCl$$

after the completion of which, very little further reaction occurs, then the simultaneous disappearance of equal pressures of toluene and chlorine is accounted for. It might, however, be suggested that this does not eliminate the possible production of other, more highly chlorinated <u>substitution</u> compounds. The absence of an appreciable pressure change during the thermal reaction suggests that no non-volatile products are formed, such as the more highly chlorinated addition and substitution compounds, e.g. benzal chloride would liquify out, and cause a distinct decrease in pressure. Taking these two facts in conjunction, the above equation is believed to express satisfactorily the main chemical change occurring during the thermal reaction.

Conclusion:

1. While Mason et alia[53] observed the presence of a thermal reaction at temperatures of 250°C and above, it has been found that a considerable thermal reaction takes place at 25°C between chlorine and toluene in the gaseous phase. The value of the velocity constant, k, has been found to be in the region of 8.2×10^{-23} (concentration of reactants measured in molecules, and time in seconds). Experimental results were not as reproducible as desired. Surface action is probably the controlling factor.

2. A mechanism of the thermal reaction has been submitted, which explains its almost complete cessation after 20-30 minutes. It is suggested that the toluene present is converted almost entirely to benzyl chloride, but that no further substitution or addition occurs.

3. The presence of this thermal reaction considerably complicates the examination of the photo-reaction. It is found empirically that 20 seconds after the chlorine has been completely introduced into the reaction vessel, approximately one-sixth of the chlorine (and presumably one-third of the toluene, if the previous mechanism is correct) has reacted. This change is not due to an abnormally high rate of reaction, but to the time interval which must, of necessity, occur, during the introduction of the reacting materials. It is, however, too large a change to permit the usual methods of examining the photo-reaction to be applied in this case.

PHOTO-REACTION IN THE OXYGEN-FREE SYSTEM.

As has been seen, the presence of a thermal reaction considerably complicates the examination of the corresponding photo-reaction.

However, two observations were made on the rate of the total reaction, thermal plus photo-. 15 mm of toluene were introduced into the reaction vessel, 30 mm of chlorine then added, and illumination immediately commenced. The light-spot on the galvanometer scale was read at various time intervals and hence an approximate value of the chlorine concentration found, at any instant.

The pressure of the gas mixture, which was registered on the Bourdon gauge during illumination, is of interest. When the light was first passed, an increase in pressure immediately occurred, but after about 10 seconds, the gauge pointer became stationary and then the pressure gradually decreased, the pointer passing the original zero position another 10 seconds later, and continuing to move slowly in the same direction for some minutes.

This pressure variation can be explained thus: the first increase is due to the presence of the Draper effect, i.e. the heat evolved by the exothermic reaction, increasing the gas pressure. When the pressure ceases to increase and starts decreasing, another effect is evident. It has previously been noted by Olivier,[50] and Kharasch and Berkman,[51] that not only does substitutional reaction between toluene and chlorine occur in light, but also addition reaction in the nucleus. Were substitution reaction occurring alone, the pressure would remain constant, assuming, of course, that the product were sufficiently volatile to remain in the gas phase.

i.e. $\mathrm{X.H} + \mathrm{Cl_2} \longrightarrow \underset{\text{(volatile)}}{\mathrm{X.Cl}} + \mathrm{HCl}$

When addition reaction also occurs, the chlorine reacts without producing compensatory HCl to keep the volume and pressure of the gas mixture at the original value. Also, the addition products of toluene, necessarily nuclear, are comparatively non-volatile, and it would hence be expected that a deposit would occur inside the reaction vessel. This was found to be the case - there remained a tarry organic residue, which could be removed with alcohol. It has been previously noted that this residue was not obtained during the thermal observations, suggesting in that instance, no addition, only substitution, of chlorine occurring in the toluene molecule.

This experimental procedure has two disadvantages.

1. Due to the initial rapid rate of reaction, the galvanometer spot moves quickly. Until the

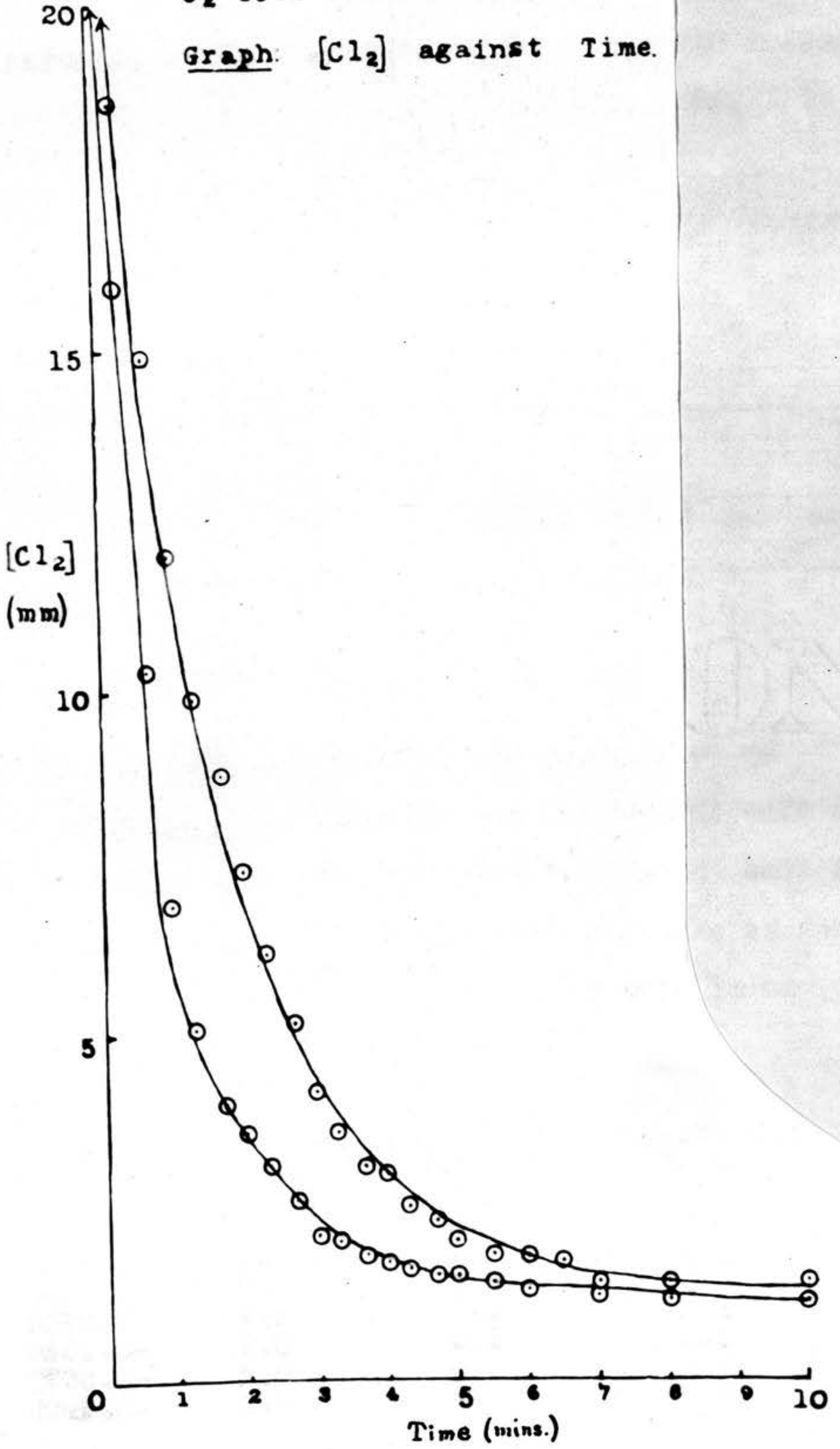
reaction becomes less rapid, a slight time-lag in the galvanometer readings must be expected, i.e. there will be a tendency for values of I, the transmitted intensity, when substituted in the $\log_{10}\frac{I_0}{I}$ factor and taken in conjunction with the calibration graph, to give corresponding values of the chlorine concentration, higher than actually present. In effect, the reaction rate will be slightly faster than the galvanometer reading suggests.

2. When the light is first switched on, the galvanometer spot takes a finite time to move from its zero position to a real value.

Either possible source of error can be considered of a negligible size after reaction has proceeded for 60 seconds. As the rate of reaction is still comparatively large after this time-interval, extrapolation to zero time can be carried out, with a good degree of accuracy.

O$_2$-free Total Reaction

Graph. [Cl$_2$] against Time.



<u>Total Reaction</u>: Thermal + Photo-.

Reaction Mixture: 15 mm toluene + 30 mm chlorine.

λ of light: 365 mu.

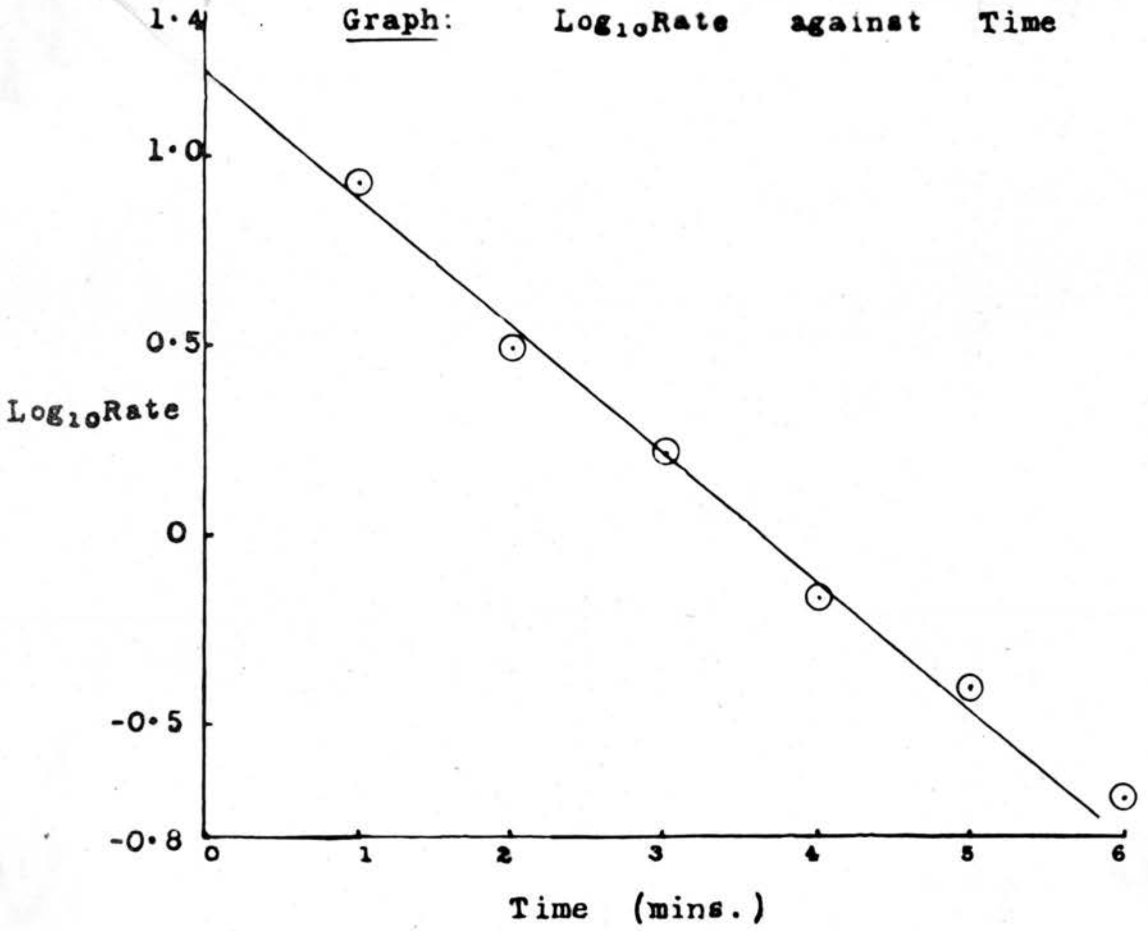
	I_0	Time (mins.)	0	$\frac{1}{3}$	$\frac{2}{3}$	1
Observation I	38.2	$[Cl_2]$	30.0	18.6	14.9	12.0
II	38.2	mm.	30.0	15.9	10.3	6.9

	Time	$1\frac{1}{3}$	$1\frac{2}{3}$	2	$2\frac{1}{3}$	$2\frac{2}{3}$	3	$3\frac{1}{3}$	$3\frac{2}{3}$	4
I	$[Cl_2]$	9.9	8.8	7.4	6.2	5.2	4.3	3.6	3.1	3.0
II		5.1	4.0	3.6	3.1	2.6	2.1	2.0	1.8	1.7

	Time	$4\frac{1}{3}$	$4\frac{2}{3}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7	8	10
I	$[Cl_2]$	2.5	2.3	2.0	1.8	1.8	1.7	1.4	1.4	1.4
II		1.6	1.5	1.5	1.4	1.3	1.3	1.2	1.1	1.1

By estimating the rate of the reaction at various time intervals, and plotting the $\log_{10}$ rate against time, an almost straight line is obtained, which can be extrapolated to zero time, again with a good degree of accuracy.

Time (mins)	Observation I Rate mm./min.	Observation II Rate mm./min.	Mean.	$\log_{10}$ Rate.
1	9.1	8.4	8.8	0.9445
2	2.9	3.4	3.2	0.5051
3	1.1	2.2	1.7	0.2304
4	0.3	1.0	0.7	-0.1549
5	0.2	0.6	0.4	-0.3979
6	0.2	0.2	0.2	-0.6990



Graph: $\log_{10}$Rate against Time

A value is thus obtained of the total rate of reaction, thermal + photo-, at zero time. By again assuming that the total rate can be regarded as the sum of the thermal + photo-, and subtracting the previously estimated value of the thermal reaction (2.25 mm per minute), the rate of the photo-reaction alone at time = 0 can be found.

From the value of the incident light intensity a measure of the absorbed light intensity can be found, and thus the quantum efficiency deduced for zero time.

At time = zero.

$\log_{10}$ Rate = 1.22 (by extrapolation)

Rate of total reaction = 16.6 mm per minute.

Rate of thermal reaction = 2.25 mm per minute.

Rate of photo-reaction alone = 14.35 mm per minute.

$I_0 = 38.2$ cms. $\quad\therefore I_{abs} = 14.9$ cms.

$$\therefore \text{Relative } \gamma_{Cl_2} = \frac{14.35}{60 \times 14.9}$$

$$\underline{0.0161}$$

$$\therefore \gamma_{Cl_2} \text{ absolute } = \underline{7.35 \times 10^4} \text{ quanta/second.}$$

Conclusion.

A measure of the magnitude of the quantum efficiency of the photo-reaction between toluene and chlorine has been obtained. The presence of an accompanying thermal reaction was taken into account.

On illuminating a mixture of 15 mm toluene and 30 mm of chlorine, by light of wavelength 365 mu and absolute intensity 8.59 x 10^{14} quanta per second, the value of γ_{Cl_2} was found to be 7.35 x 10^4 molecules per quantum of light absorbed.

Part III. THE PRIMARY PHOTO-REACTION BETWEEN METHANE AND CHLORINE

Introduction.

Many analogies can be drawn between the chemical behaviour of hydrogen gas and methane gas. In particular, they both react with chlorine forming the corresponding chlorides, and when this occurs in the presence of light, the reaction in either case is very rapid, indicating the presence of a chain mechanism of high quantum efficiency. Whereas the photo-chlorination of hydrogen has been exhaustively examined in the past, surprisingly little investigation has been made into the photo-reaction with methane.

Using the present type of apparatus, which had proved very successful in yielding reproducible results with the hydrogen-chlorine reaction, an examination of the photo-reaction between chlorine and methane in the gas phase, was carried out. The effect on the quantum efficiency of the variation of chlorine pressure, methane pressure, and the absorbed light intensity, and the effect of the addition of varying pressures of oxygen, nitrogen, and hydrogen chloride have been examined in detail.

Except for a simple determination by Berthelot[54] of the quantity of methyl chloride produced by mixing methane and chlorine in diffused day-light, the only other early examination of the photo-reaction was made by Whitson,[55] to determine its technical possibilities for the production of methyl chloride. Employing an apparatus, not dissimilar to the one used in the present investigation, he determined the methyl chloride formed, by freezing it out and measuring the residual gases. The inhibitory action of nitrosyl chloride was observed. However, it was concluded that the yields were not sufficient to make the process an economic proposition.

The first actual determination of the quantum efficiency of the reaction was made by Coehn and Cordes,[56] when they examined, not only the photo-reaction between chlorine and methane, but also between chlorine and CH_3Cl, CH_2Cl_2, $CH\,Cl_3$ respectively. They found that the quantum efficiencies in each case were of the same order of magnitude. In the case of methane, in particular, the value of γ, on initial exposure to light, was found to be of the order 1.6×10^4 molecules per quantum, where the proportion of methane to chlorine was 1:1. In this reaction the products formed, other than HCl, were CH_3Cl, CH_2Cl_2, $CH\,Cl_3$, and CCl_4. No chloroethanes were detected. As has been confirmed in the present investigation, it was found that the effect of impurities was very marked indeed.

Various chain mechanisms are discussed, and finally the reactions

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$

$$Cl + CH_4 \longrightarrow CH_3 + HCl$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

were proposed, in preference to the reaction

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$

$$Cl + CH_4 \longrightarrow CH_3Cl + H$$

$$H + Cl_2 \longrightarrow HCl + Cl$$

This decision was arrived at from a consideration of the separate heats of the various reactions.

Jones and Bates,[57] in a short paper, also considered the previous two mechanisms, and carried out observations in order to differentiate between them. Using a flow system, they worked under the immediate disadvantage that both their chlorine and methane contained a small amount of oxygen - 0.25% and 0.8% respectively.

However, illuminating with a Pyrex mercury arc, they obtained observations at three temperatures, 5°C, 25°C, and 45°C, measuring the residual chlorine and HCl volumetrically.

Using an analogous equation to Thon's,[33] for the hydrogen-chlorine reaction,

$$\frac{d[CH_3Cl]}{dt} = \frac{K[CH_4][Cl_2]^2}{[O_2]\left(k[CH_4]+[Cl_2]\right)}$$

they found that K was constant, if the $CH_4 - Cl_2$ ratio was varied, only when k = 1, instead of = 10, as in the case of the hydrogen-chlorine reaction.

They finally conclude that, of the two mechanisms originally suggested by Coehn and Cordes,[56] that involving the CH_3 radical is the more suitable. Were chlorine to react with methane to produce directly methyl chloride and hydrogen atoms, it can be visualised that a chlorine atom, on approaching one of the triangular faces of the carbon tetrahedron of methane, would interact with the three hydrogen atoms at the apices of the triangle, and would produce a strong repulsion, as the chlorine atom requires a high activation energy for reaction to occur. If, however, the chlorine atom approaches along the line of the C-H bond, it might react with the single hydrogen atom to produce CH_3 and HCl. This would require a much lower activation energy, due to its large distance from the other three hydrogen atoms.

Also, if hydrogen atoms were formed during the reaction, it would be expected that small amounts of H_2O_2 and H.CHO would be formed. On testing for these substances in the reaction mixture, no trace of either was found.

A more rigorous examination of the reaction velocity was carried out by Tamura[58], using a method of thermal analysis. In this case, great care was taken to exclude impurities, especially oxygen, to as great an extent as possible. A good degree of reproducibility of the results was claimed.

The actual observations made, were direct measurements of the reaction velocity of a mixture of methane and chlorine at a total pressure of 390 mm. The only variable was the intensity of the incident light, - three values were employed.

Tamura found the reaction velocity to be proportional to a power of I_{abs} approaching 0.5, and concluded that the reaction chains are terminated mainly by mutual recombination of chain carriers, rather than by inhibitors or on the walls of the vessel.

He estimated the mean life of the reaction chains and the quantum efficiencies under the given conditions.

On calculating the collision yield of the reaction:

$$Cl + CH_4 \rightarrow CH_3 + HCl$$

and assuming certain values of the dimensions of the particles involved, the energy of activation was found to be not greater than 6.2 kilocals, - the maximum value for the rate determining partial reaction.

The alternative possibility for the above reaction:

$$Cl + CH_4 \longrightarrow CH_3Cl + H$$

is endothermic by about 21 kilocals., and hence this reaction cannot be considered as a partial reaction in the final mechanism.

Calculation of the life of a chlorine atom showed that the reaction:

$$Cl + Cl + M \longrightarrow Cl_2 + M$$

was not of importance. But assuming the formation of Cl_3 molecules, followed by their removal by various mechanisms, a good agreement was obtained for the values of their existence-times in theory and experimentally.

Tamura finally put forward his own scheme of reaction, the main features being the assumption of the particles, CH_3 and Cl_3, as unstable intermediates.

$$Cl_2 \longrightarrow Cl + Cl'$$

$$Cl + CH_4 \longrightarrow CH_3 + HCl$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

$$Cl + Cl_2 + M \longrightarrow Cl_3 + M$$

$$Cl_3 + M \longrightarrow Cl + Cl_2 + M$$

$$Cl_3 + Cl_3 \longrightarrow 3Cl_2$$

$$Cl + Cl_3 \longrightarrow 2Cl_2$$

$$Cl \longrightarrow \text{surface}$$

$$Cl_3 \longrightarrow \text{surface}$$

Experimental Note.

Due to the entirely gaseous nature of the reaction, greater ease of manipulation of the various reagents was possible, compared with the case of the chlorine-toluene reaction. An important precaution for the elimination of inhibitors - namely, the preliminary "washing" of the reaction vessel with chlorine, - could now be put into effect. This was actually carried out in each case, before adding any other gas to the reaction vessel. A check on the degree of sensitivity of the photronic cell-galvanometer system was also able to be made at each observation, when the chlorine concentration was determined from the $\log_{10}\frac{I_0}{I}$ graph, and compared with the manometer reading.

As expected with an exothermic reaction, such as that between chlorine and methane, an effect was observed, corresponding to the Draper effect in the hydrogen-chlorine reaction. An important indication of the degree of purity of the reactants was given by noting the size of this effect on first illuminating the gas mixture. A typical case with a gas mixture of 50 mm methane and 50 mm chlorine, on illumination with 365 mu light, and $I_{abs} = 7.9 \times 10^{13}$ quanta per second, was to give an increase in pressure of 1.1 mm. The size also gave a rough indication of the reaction rate, and hence a suitable length of time of illumination.

The observations in this investigation were carried out in a cylindrical silica vessel of volume, 21.74 ml., the light entering and leaving through the plane-sided faces of the cell. Unlike the case of the chlorine-toluene reaction, no deposit was observed to have formed at any stage in the investigation indicating the essentially volatile nature of the reaction products.

Also unlike the chlorine-toluene reaction, when the existence of a thermal reaction between chlorine and methane at the temperature of the investigation (25°C) was early examined, it was found to be completely absent. Gas mixtures containing 50 mm CH_4 - 50 mm Cl_2, and 100 mm CH_4 - 100 mm Cl_2 were left in the darkened reaction vessel for 30 minutes and 1 hour respectively, after which the chlorine concentration was found to be identical to the initial value. At higher temperatures (250°C) Pease and Waltz[59] have observed that a thermal reaction does take place to a considerable extent, and that it possesses a mechanism of the chain type.

One set of readings was carried out in the presence of HCl gas. Instead of introducing the previously-purified gas, it was prepared in the reaction vessel itself, by illuminating, at first cautiously and then using white light, measured quantities of hydrogen and chlorine. In this way, the purity of the resultant gas was proved by the size of the corresponding Draper effect. The order of introduction of the hydrogen and chlorine into the reaction vessel was of importance. Chlorine was the first gas to be introduced, then the hydrogen, and finally more chlorine. In that way, it was intended that all the hydrogen would be "washed" into the vessel and converted to HCl. Sufficient chlorine was added to convert the hydrogen to HCl and also to react later with the methane.

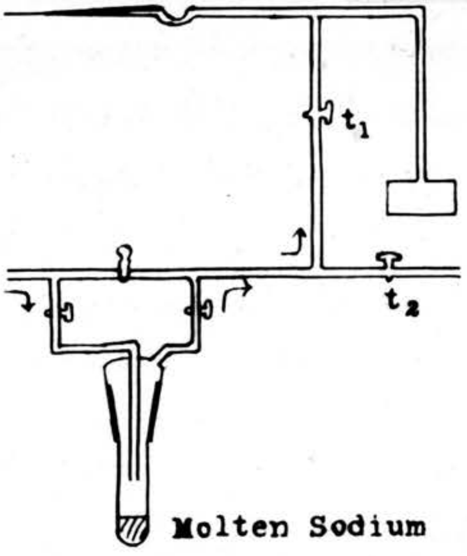
A point arose from this procedure which obviously involves large chlorine pressures. It was found that if the amount of chlorine was determined using the photocell-galvanometer system after reaction with the hydrogen was complete, a slightly lower concentration was recorded than expected. This discrepancy was finally traced to the order of entry of hydrogen and chlorine, hence determining which gas would remain in the connecting tubes, and was corrected for by measuring the chlorine concentration immediately before reacting with methane. The size of the discrepancy would obviously have been smaller, had the volume of the reaction vessel been larger than 21.74 ml.

The purification of methane has been described in the main experimental section. As the procedure was lengthy, requiring extreme care at each stage to prevent the introduction of inhibitors, a comparatively large volume (4 litres) was collected at one time. The procedure was actually carried out twice during the investigation.

The two samples were found to differ only slightly in their degree of purity, as determined by the quantum efficiencies of similar mixtures with chlorine. It was thought that by passing the gas, first through, and then over, molten sodium, the last traces of oxygen - the most probable inhibitor - would be removed. However, when the extreme sensitivity of the gas mixtures to small pressures of oxygen was observed, the possibility that a trace of oxygen might yet be present in the methane had to be considered.

The possibility was again suspected, after determining the effect of variation of methane concentration on the quantum efficiency of the reaction. It was found that, with both samples of methane, the quantum efficiency decreased with increasing methane concentration. This can be very readily explained by the presence of a trace of an inhibitor, such as oxygen, which becomes increasingly effective, the greater the concentration of methane present.

As a final attempt to destroy inhibitors, without allowing time for their regeneration, the small

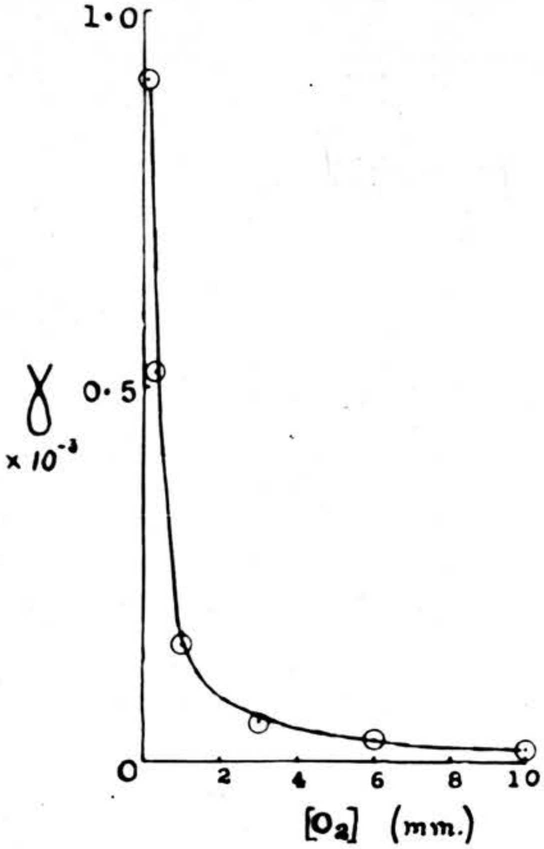

t1
t2
Molten Sodium

sodium trap, as in the diagram opposite, was incorporated in the main gas line.

Immediately before introducing methane into the reaction vessel, any gases above the molten sodium were removed by a short evacuation, and the taps so arranged that the methane had to pass over the sodium, before directly entering the reaction vessel. As can be seen from the appropriate graph, using this technique, the quantum efficiency tended to approach a constant maximum value as the methane concentration increased.

Graph:

γ against $[O_2]$



Results:

Table 1. Variation of γ with $[O_2]$.

λ of light: 365 mu.

$[O_2]$ mm.	Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 mm.	Time secs.	I_{abs} relative cm.	γ relative	γ absolute $\times 10^{-3}$	$\gamma \times [O_2] \times 10^{-3}$
0.1	45.9	45.8	8.2	80	10.3	0.0100	0.913	0.0913
0.25	46.5	46.5	7.1	120	10.4	0.00569	0.522	0.131
1.0	45.0	45.0	10.0	600	10.2	0.00167	0.153	0.153
3.0	46.8	46.7	6.7	1200	10.4	0.000537	0.0493	0.148
6.0	45.8	45.7	8.7	3000	10.2	0.000283	0.0260	0.156
10.0	44.1	44.0	12.0	7200	10.0	0.000167	0.0153	0.153
	On addition of 200 mm HCl.							
6.0	46.1	46.0	9.1	3000	10.2	0.000297	0.0273	-

Graph 1.

Graph: $\gamma \times [O_2]$ against $[O_2]$

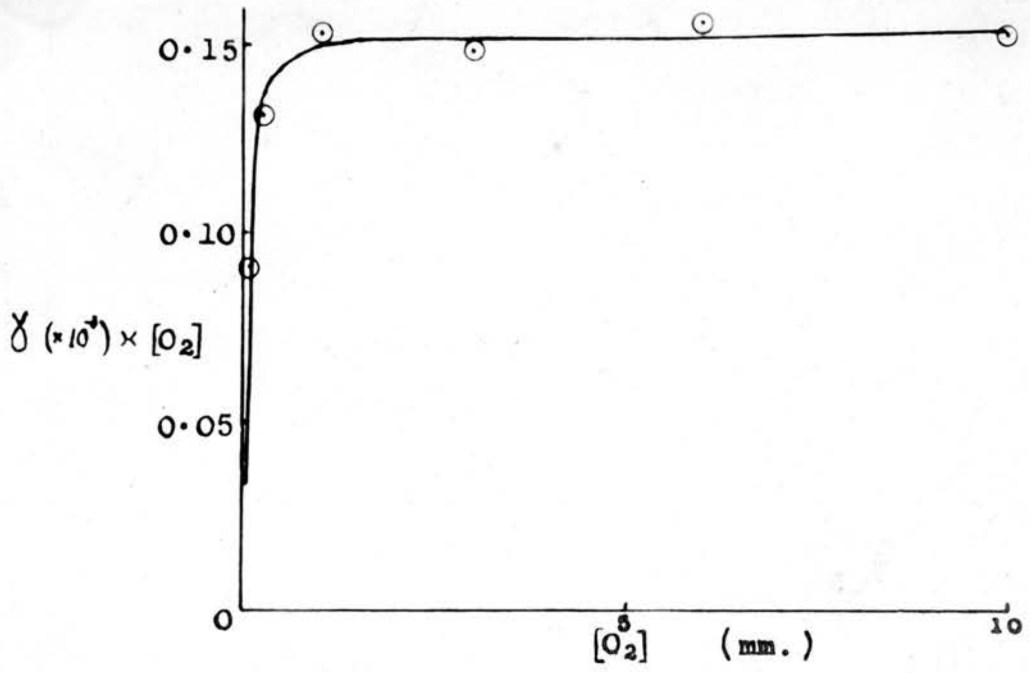


Table 2. **Variation of γ with I_{abs}.**

λ of light: 365 mu and 406 mu.

λ mu	Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 mm.	Time secs.	I_{abs} relative cm.	$I_{abs} \times 10^{-13}$ quanta/sec.	γ relative	γ absolute $\times 10^{-3}$
365	45.7	45.5	9.0	40	10.2	7.87	0.0221	2.02
365	45.1	45.1	9.8	40	10.2	7.87	0.0240	2.20
365	45.3	45.3	9.5	40	10.2	7.87	0.0233	2.14
365	44.1	44.0	12.0	80	5.8	4.48	0.0259	2.37
365	44.8	44.8	10.5	420	0.98	0.757	0.0255	2.34
365	45.4	45.4	9.3	600	0.52	0.402	0.0298	2.73
406	44.4	44.5	11.0	800	0.86	0.277	0.0160	3.52
406	44.4	44.4	11.2	1000	0.54	0.174	0.0207	4.56
365	43.7	43.6	12.8	600	0.185	0.143	0.115	10.58

Graph 2.

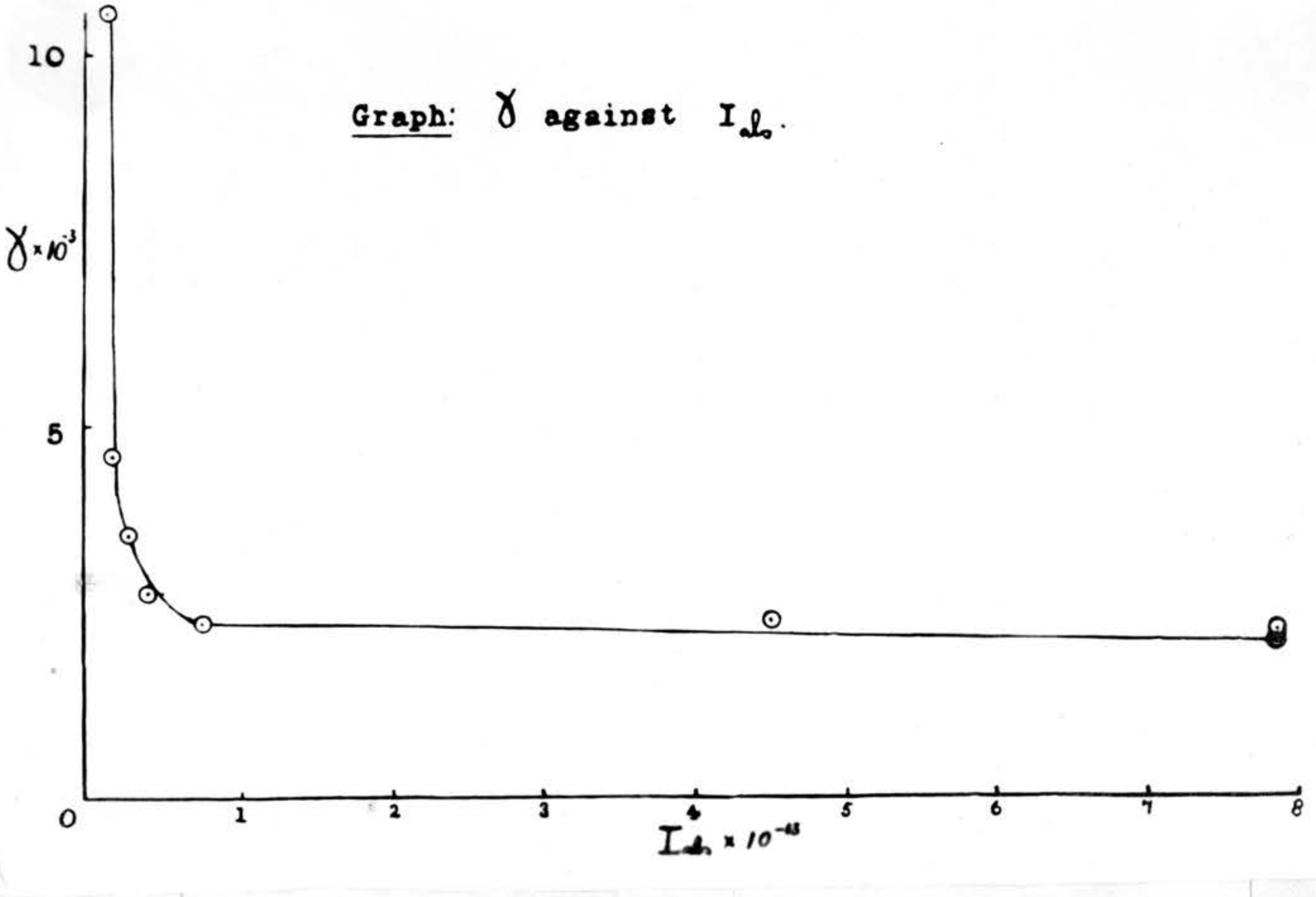


Table 3. Variation of γ with $[Cl_2]$.

λ of light: 365 mu and 406 mu.

λ mu	Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 mm.	Time secs.	I_{abs} relative cm.	γ relative	γ absolute $\times 10^{-3}$	$I_{abs} \times 10^{-13}$
365	45.9	12.2	9.3	300	1.57	0.0197	1.81	1.21
365	44.0	19.0	12.0	180	2.80	0.0238	2.18	2.16
365	44.2	44.1	11.8	70	5.81	0.0291	2.67	4.48
365	43.9	63.9	12.2	50	7.80	0.0313	2.87	6.02
365	38.7	88.7	22.6	70	10.0	0.0323	2.96	7.75
406	44.4	44.5	11.0	800	0.86	0.0160	3.52	0.277
406	42.8	92.8	14.5	300	1.66	0.0291	6.41	0.53
406	33.5	183.5	33	300	2.97	0.0370	8.15	0.96
406	25.5	275.5	49	400	4.03	0.0304	6.70	1.30
406	21.5	371.5	57	300	8.47	0.0224	4.93	2.73

Graph 3.

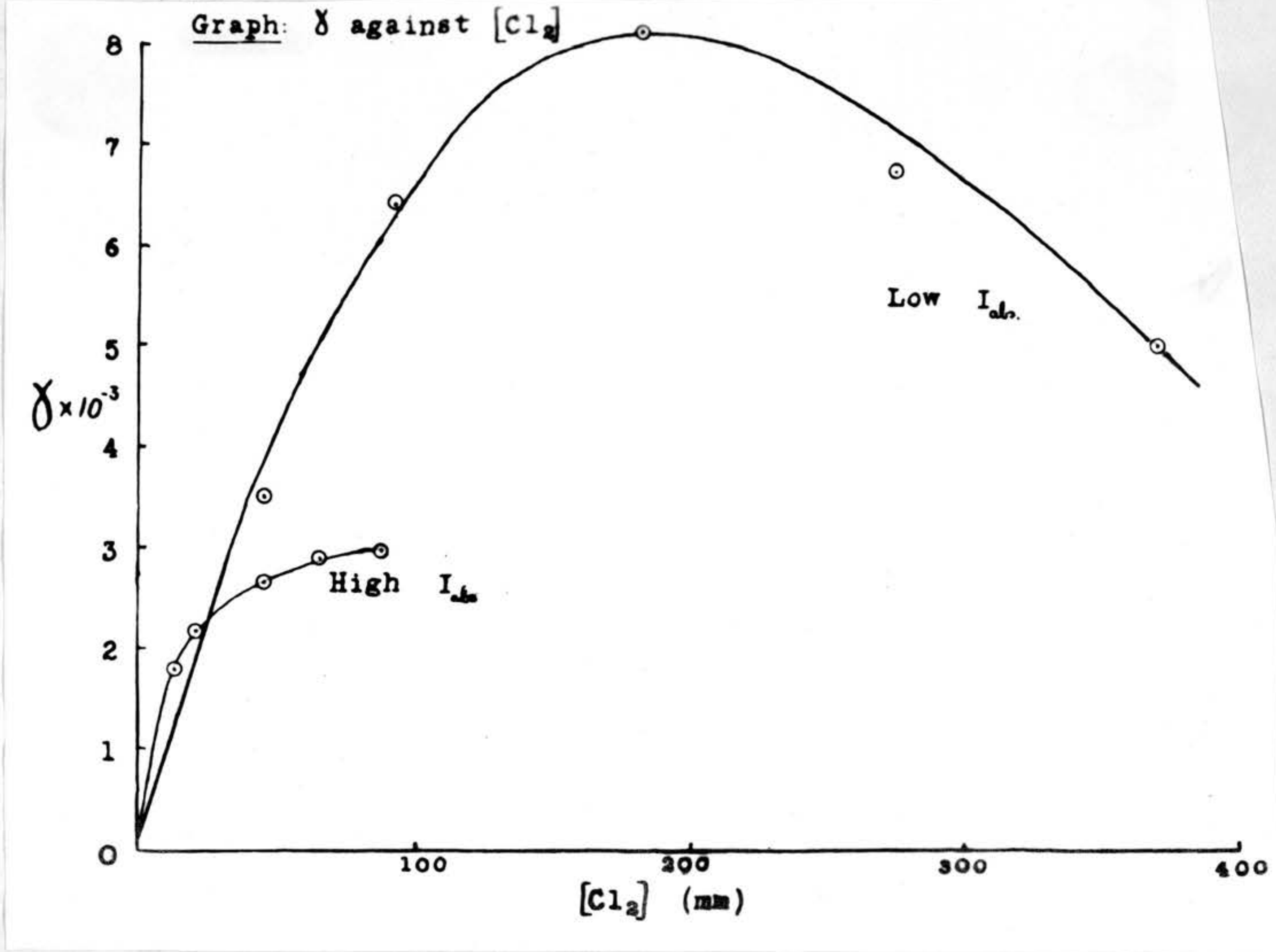


Table 4. **Variation of γ with $[CH_4]$.**

λ of light: 365 mu.

Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 mm.	Time secs.	I_{abs} relative cm.	γ relative	γ absolute $\times 10^{-3}$	$I_{abs} \times 10^{-13}$
21.2	46.2	7.7	80	6.06	0.0160	1.47	
44.0	43.9	12.0	80	5.80	0.0259	2.38	4.418
44.8	44.9	10.3	60	6.00	0.0286	2.63	
194.6	44.6	10.8	50	5.86	0.0369	3.39	
294.7	44.7	10.7	50	5.88	0.0364	3.34	
394.3	44.3	11.5	55	5.81	0.0360	3.30	

Graph 4.

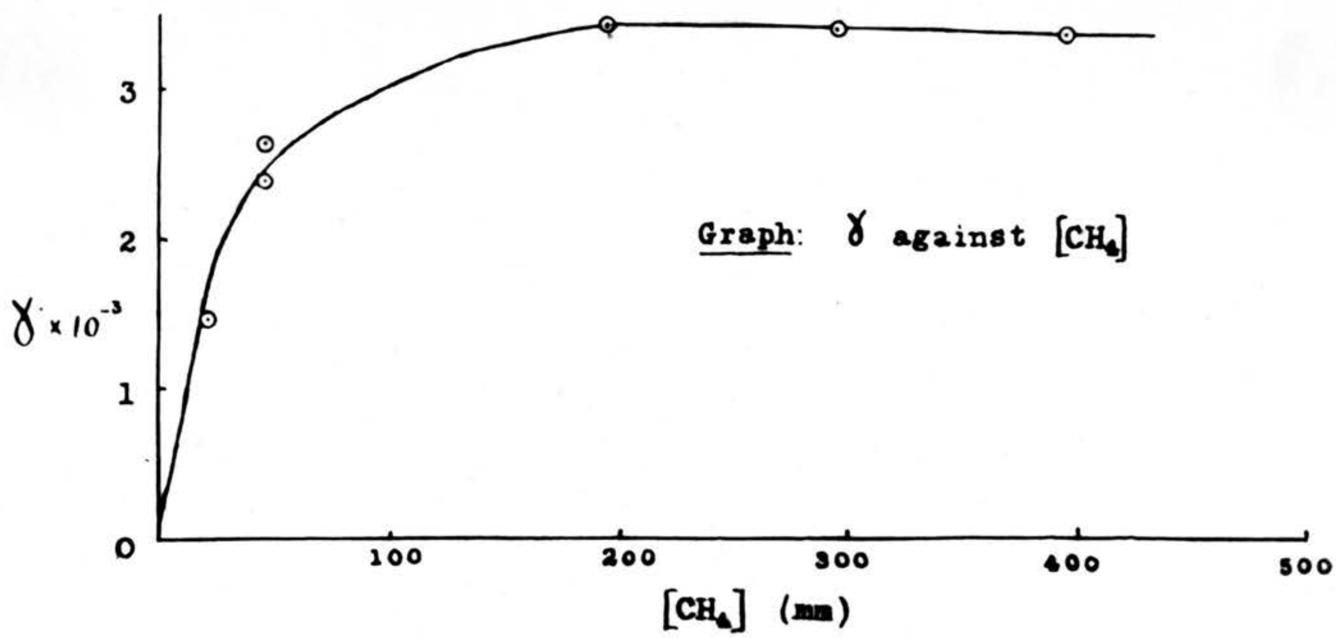


Table 5. Variation of γ with $[N_2]$.

λ of light: 365 mu.

$[N_2]$ mm.	Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 mm.	Time secs.	I_{ab} relative cm.	γ relative	γ absolute $\times 10^{-3}$
0	44.4	44.3	11.3	35	10.0	0.0323	2.96
50	45.5	45.5	8.9	35	10.4	0.0244	2.24
100	46.3	46.4	7.3	35	10.6	0.0197	1.81
200	45.8	45.8	8.3	50	10.4	0.0160	1.47
300	44.7	44.8	10.4	70	10.2	0.0146	1.34
400	46.1	46.1	7.8	70	10.5	0.0106	0.97
400	45.2	45.2	9.5	80	10.2	0.0116	1.07
0	46.7	46.8	8.3	450	0.189	0.0971	8.91
50	45.8	45.7	8.7	600	0.188	0.0771	7.08
200	47.3	47.3	7.5	750	0.190	0.0526	4.84
400	48.1	48.3	5.5	1000	0.195	0.0282	2.59
400	48.5	48.5	5.0	1200	0.197	0.0212	1.94

Graph 5.

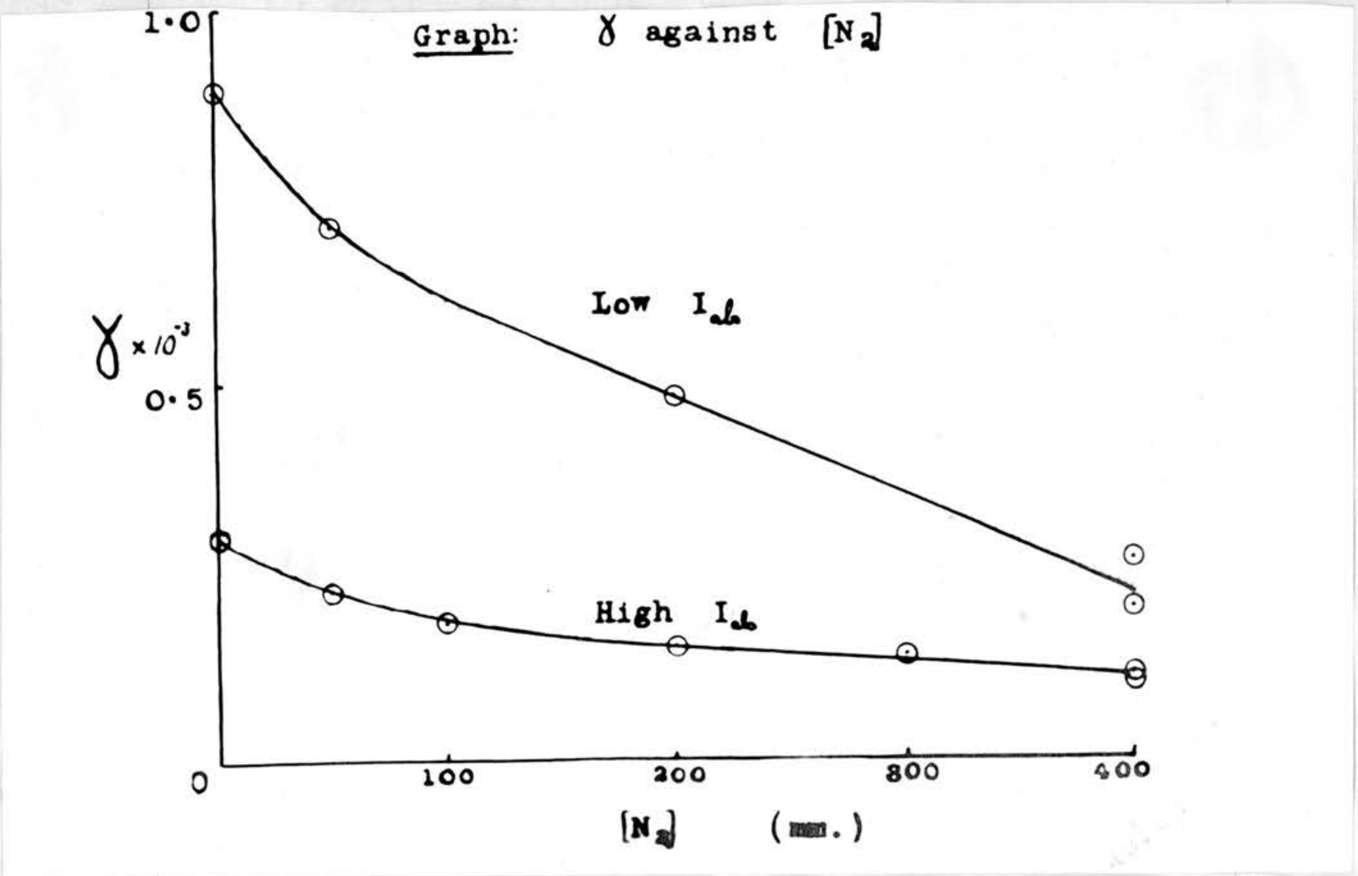
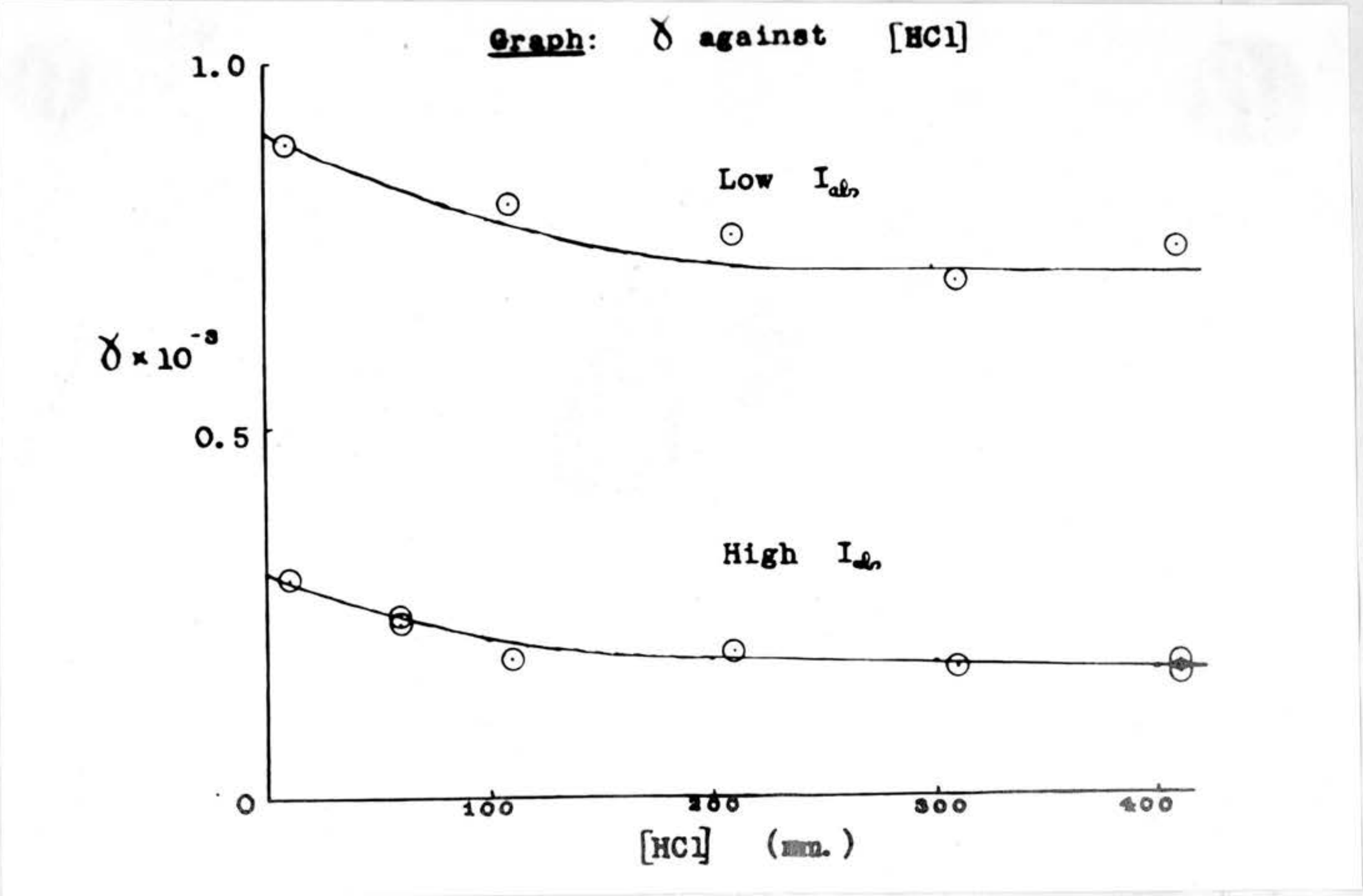


Table 6. Variation of γ with [HCl].

λ of light: 365 mu.

Added [HCl] mm.	Average $[CH_4]$ mm.	Average $[Cl_2]$ mm.	ΔCl_2 expt. mm.	ΔCl_2 corrected mm.	Time secs.	I_{abs} relative cm.	γ relative	γ absolute $x\ 10^{-3}$
50	44.5	44.5	11.0	9.0	35	10.0	0.0257	2.36
50	44.1	44.2	11.5	9.5	35	10.0	0.0271	2.49
100	44.8	44.9	10.2	7.2	35	10.2	0.0202	1.85
200	44.5	44.4	11.0	7.5	35	10.0	0.0214	1.96
300	42.7	42.7	14.5	6.3	35	9.7	0.0186	1.70
400	41.1	41.1	17.8	6.3	35	9.4	0.0191	1.76
400	41.3	41.4	17.2	5.7	35	9.4	0.0173	1.59
100	44.1	44.1	11.8	8.8	550	0.183	0.0874	8.02
200	43.3	43.4	13.2	9.7	650	0.181	0.0825	7.57
300	41.0	41.0	18.0	9.8	750	0.172	0.0760	6.97
400	38.5	38.5	23.0	11.6	900	0.160	0.0806	7.39

Graph 6.



Discussion.

It was found that experimental determinations of quantum efficiencies showed, on repetition, an average variation in magnitude not greater than 10%. This tended to ~~de~~increase immediately after the various taps on the apparatus had been newly greased, or if any particular part had been renewed or replaced.

Such a degree of reproducibility of results was considered satisfactory, and suggested the absence of any occasional inhibitors in the gas system. It also pointed to a good degree of purity of the various gases employed in the investigation. The exceptional case of methane has been referred to already. The complex procedure for its purification was the most liable to bring about the introduction of inhibitors. In previous investigations on the subject, actual percentages of oxygen present in the gas have usually been quoted, and in only one instance[58] has the claim been made that the methane was quite pure.

In the case of chlorine and nitrogen, there was no erratic behaviour in the experimental values to indicate the presence of inhibitors, and when hydrogen chloride gas was formed in the reaction vessel, the accompanying large and constant Draper effects were a good guarantee of its purity.

As the possibility cannot be entirely ruled out that a trace of oxygen was present in the gas mixtures, its effect on the quantum efficiency was examined quantitatively.

The retarding action is very large, and when the product γ x $[O_2]$ is plotted against $[O_2]$, it can be seen from the graph that the maximum on the curve, beyond which the product becomes independent of the oxygen concentration, takes place at a pressure of about 1 mm of oxygen ($[Cl_2]$ = 43 mm. $[CH_4]$ = 43 mm.). The corresponding pressure of oxygen at which this occurs in the case of the chlorine-toluene reaction (page 91) was found to be about 300 mm ($[Cl_2]$ = 25 mm. [Toluene] = 10 mm.), while Norrish and Ritchie[3] found that, with the hydrogen-chlorine reaction, it occurred at a pressure of 10 mm, under the given experimental arrangements ($[Cl_2]$ = 43 mm. $[H_2]$ = 43 mm.). Such a comparison indicates how powerful is the retarding influence of oxygen in this reaction.

As mentioned in the introduction, two possible chain mechanisms for the reaction have been examined in the past. The initial step, the dissociation of chlorine molecules into atoms by light of wavelength 365 or 406 mu, requires no discussion.

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$
$$Cl + CH_4 \longrightarrow CH_3 + HCl$$
$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$
$$Cl + CH_4 \longrightarrow CH_3Cl + H$$
$$H + Cl_2 \longrightarrow HCl + Cl$$

In every case, previous investigators have agreed, usually from considerations of the heats of the various reactions, that the chain, involving the CH_3 radical as an intermediate, is more probably the correct mechanism, than that involving a hydrogen atom.

In the kinetics, which follow, both cases were examined, and it was found each time that the same final expression was obtained. So this method does not allow any decision to be made between the two possibilities.

However, the assumption that a CH_3 radical is formed, gives a very convincing explanation of the great sensitivity of this reaction to oxygen, as compared with the hydrogen-chlorine reaction.

A point against the formation of hydrogen atoms in the system is that the quantum efficiency of a 50 mm methane - 50 mm chlorine gas mixture in the presence of 6 mm oxygen, gives an almost identical value when 200 mm of HCl are now added to a similar system.

It has been found that one effect of HCl in the hydrogen-chlorine photo-reaction, with oxygen present, is to cause a retardation, attributed to the mechanism:

$$H + O_2 + HCl \longrightarrow HO_2 + HCl$$
$$HO_2 + Cl_2 \longrightarrow HCl + ClO_2$$

No retardation is found in the analogous reaction with methane (page 119) and this provides further evidence against the presence of hydrogen atoms in the gas system.

The effect of the variation of the intensity of absorbed light on the quantum efficiency, showed that it decreased rapidly with increasing values of I_{abs} until a value was reached, beyond which it became independent of I_{abs}. The two values of the quantum efficiency using light of $\lambda = 406$ mu closely fit the curve, obtained from determinations with 365 mu light.

If the rate of reaction is expressed by an equation of the type:

$$-\frac{d[Cl_2]}{dt} = k\, I_{abs}^{\,n}$$

$$\gamma_{Cl_2} = \frac{-\frac{d[Cl_2]}{dt}}{I_{abs}}$$

then values of "n" can be deduced from the equation:

$$1 - n = \frac{\log_e \gamma_1 - \log_e \gamma_2}{\log_e I_{abs_2} - \log_e I_{abs_1}}$$

The following values of "n" were obtained in this way:

$I_{abs} \times 10^{-13}$ quanta/sec.	$\gamma \times 10^{-3}$ mols./$h\nu$	n
8.0	2.25	
4.0	2.30	0.97
1.0	2.45	0.95
0.5	2.80	0.81
0.4	3.00	0.69
0.3	3.40	0.56
0.2	4.10	0.54

It is seen that, over a wide range of I_{abs}, there is a definite trend in the values of the indices from almost unity at high I_{abs} to slightly above 0.5 at low I_{abs}. This same result was obtained by earlier investigators in the corresponding reaction between hydrogen and chlorine.

The effect was explained by Bodenstein[7] as due to the system of filter arrangements, used to cut down the light intensity, and hence I_{abs}. This explanation has now been denied (page 39) and the observed variation of quantum efficiency with I_{abs} must be interpreted in some other way.

The effect of variation of chlorine pressure showed an initial increase in quantum efficiency with increasing chlorine concentration, followed by a decrease, at pressures above 200 mm. In order to observe changes in chlorine concentration at pressures above 100 mm, it was necessary to use light of $\lambda = 406$ mu.

At such high pressures, the same degree of accuracy in measuring the chlorine concentration cannot be obtained as at pressures below 100 mm, using light of $\lambda = 365$ mu.

The effect of the addition of various pressures of the two inert gases, nitrogen and hydrogen chloride, was similar. At both high and low values of I_{abs}, increasing pressures of the inert gases slightly decreased the quantum efficiency, the effect being somewhat greater in the case of nitrogen, than with hydrogen chloride.

Values of "n" were determined, as in the previous case, for gradually increasing pressures of the inert gases.

[HCl] mm.	γ ($I_{abs} = 79.62 \times 10^{12}$)	γ ($I_{abs} = 1.48 \times 10^{12}$)	n
0	3030	9050	0.73
100	2110	7820	0.67
200	1810	7230	0.65
300	1790	7150	0.65
400	1770	7070	0.65

$[N_2]$ mm.			
0	2960	8910	0.72
100	1890	6100	0.71
200	1510	4750	0.71
300	1290	3500	0.75
400	970	2590	0.73

In this instance, it can only be said that a slight change in "n" occurs over a large range of inert gas pressure.

In considering possible mechanisms of this reaction between methane and chlorine, it has been assumed that the main product formed is methyl chloride: to that end, the times of illumination have been kept small, when possible, to minimise further substitution. Coehn and Cordes[56] showed that the quantum efficiencies of photo-reactions between chloro-substituted compounds of methane and chlorine were high, - in the case of the photo-chlorination of methyl chloride, almost as high as with methane itself. However, it is considered that the assumption that mono-chlorination takes place predominantly is justified by the similarity of the trends shown by this reaction, and the corresponding photosynthesis of HCl.

It would appear that the interpretation of the results may be approached in two main ways. The fact that the rate of reaction tends to become proportional to the square root of the absorbed light intensity, under certain conditions, suggests that chain-ending may occur, either by mutual recombination of chlorine atoms or CH_3 radicals, by the reactions

$$Cl + Cl + M \longrightarrow Cl_2 + M$$

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

or by $CH_3 + Cl \longrightarrow CH_3Cl$

It is fairly certain that the first of these reactions would require a third molecule as a stabiliser or energy remover: in the second and third reaction, the complexity of the resultant molecule may render the presence of a triple collision unnecessary. On the other hand, indices of I_{abs} approaching 0.5 may be achieved by the mechanism

$$Cl + Cl_2 + M \longrightarrow Cl_3 + M$$

$$Cl_3 + M \longrightarrow Cl + Cl_2 + M$$

$$Cl_3 + Cl_3 \longrightarrow 3Cl_2$$

This has been already envisaged by Ritchie and Taylor[5] as applying to the hydrogen-chlorine reaction. In both these general mechanisms, the possibility of diffusion and convection of chain carriers to the wall must be considered.

The overall reaction is exothermic:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl + 23{,}000 \text{ cals.}$$

and at high rates of reaction, increased convection will tend to facilitate surface removal of chain carriers.

Since the corresponding heat liberated in the case of the hydrogen-chlorine reaction is 44,000 cals, the effect of convection might be less pronounced in this case.

Consider first the following reaction mechanism:

$$Cl_2 \xrightarrow{h\nu} Cl + Cl \qquad k_1$$
$$Cl + CH_4 \longrightarrow CH_3 + HCl \qquad k_2$$
$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl \qquad k_3$$
$$Cl + Cl + M \longrightarrow Cl_2 + M \qquad k_4$$
$$Cl \longrightarrow \tfrac{1}{2}Cl_2 \qquad S$$

where S represents surface removal of chlorine atoms either by diffusion or convection. Applying the Bodenstein stationary state method, we have

$$\frac{d[Cl]}{dt} = k_1 I_{abs} - k_2[Cl][CH_4] + k_3[CH_3][Cl_2] - k_4[Cl]^2[M] - S[Cl] = 0$$

$$\frac{d[CH_3]}{dt} = k_2[Cl][CH_4] - k_3[CH_3][Cl_2] = 0$$

and hence $k_4[Cl]^2[M] + S.[Cl] - k_1 I_{abs} = 0$

$$\therefore [Cl] = \frac{-S + \sqrt{S^2 + 4k_1 I_{abs} k_4 [M]}}{2k_4[M]}$$

The sign before the square root must be positive, since the chlorine concentration must be positive.

The quantum efficiency of Cl_2 removal is large, and since the complete reaction is accomplished by the chain reactions, 2 and 3, the rate of disappearance of Cl_2 is given by:

$$-\frac{d[Cl_2]}{dt} = \frac{1}{2}\left(\frac{d[CH_3Cl]}{dt} + \frac{d[HCl]}{dt}\right)$$

$$= \frac{1}{2}\left(k_2[Cl][CH_4] + k_3[CH_3][Cl_2]\right)$$

$$= k_2[Cl][CH_4]$$

$$= \frac{k_2[CH_4]}{2k_4[M]}\left[\sqrt{S^2 + 4k_1 I_{abs} k_4[M]} - S\right]$$

$$\gamma_{Cl_2} = \frac{-\frac{d[Cl_2]}{dt}}{I_{abs}}$$

$$= \frac{k_2[CH_4]}{2k_4[M]} \frac{\left[\sqrt{4k_1 k_4[M] I_{abs} + S^2} - S\right]}{I_{abs}}$$

The $K_4[M]$ terms are composite, in the sense that each of the molecules present in the system may play the part of a stabilising third molecule in the triple collision of reaction 4.

It is first noted that if surface removal of chlorine atoms is negligible, the expression reduces to

$$\gamma_{Cl_2} = \frac{k_2[CH_4]}{\sqrt{k_4[M]}} \frac{\sqrt{k_1}}{\sqrt{I_{abs}}} \qquad \text{(Equation A)}$$

This would mean that, for all intensities, the rate of reaction would be proportional to $I_{abs}^{\frac{1}{2}}$, contrary to experiment. Hence this simple mechanism does not explain the results.

Next, considering the extreme case when all the chain carriers are removed by surface action by the mechanism:

$$\begin{array}{lr} Cl_2 \xrightarrow{h\nu} Cl + Cl & k_1 \\ Cl + CH_4 \longrightarrow CH_3 + HCl & k_2 \\ CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl & k_3 \\ Cl \longrightarrow \tfrac{1}{2}Cl_2 & S \end{array}$$

we have

$$\frac{d[Cl]}{dt} = k_1 I_{abs} - k_2[Cl][CH_4] + k_3[CH_3][Cl_2] - S.[Cl] = 0$$

$$\frac{d[CH_3]}{dt} = k_2[Cl][CH_4] - k_3[CH_3][Cl_2] = 0$$

hence $S[Cl] = k_1 I_{abs}$ $\qquad \therefore [Cl] = \dfrac{k_1 I_{abs}}{S}$

Then $$-\frac{d[Cl_2]}{dt} = \frac{1}{2}\left(k_2[Cl][CH_4] + k_3[CH_3][Cl_2]\right)$$

$$= k_2[Cl][CH_4]$$

$$= \frac{k_2[CH_4]\,k_1 I_{abs}}{S}$$

and $$\gamma_{Cl_2} = \frac{k_1 k_2 [CH_4]}{S} \qquad \text{(equation B)}$$

If S is determined solely by diffusion, the value of S will remain constant for all values of I_{abs}, and the quantum efficiency will then become independent of I_{abs}. Experimentally, the quantum efficiency is proportional to $I_{abs}^{-\frac{1}{2}}$ for low intensities, becoming independent of I_{abs} at high intensities. At first sight, it might appear that with changing I_{abs}, the conditions alter, so that the chlorine atom recombination mechanism holds at low intensities, and the surface removal by diffusion at high intensities. This is, however, contrary to theoretical expectation: when the chlorine atoms are removed by two possible processes, one proportional to the square of the Cl concentration, and the other directly proportional to the concentration, then at high I_{abs}, the former will be favoured and the rate, proportional to I_{abs} at low intensities, will become proportional to $I_{abs}^{\frac{1}{2}}$ at high intensities, again contrary to the present experiments. This change in index to $n = \frac{1}{2}$ at high intensities has been recorded in the hydrogen-bromine photocombination.[60]

If S is determined mainly by convection, and again, surface removal of chain carriers is predominant, the convection S will increase as I_{abs} is increased, due to the increased rate of reaction and the consequent increase in heat evolution. The quantum efficiency will then show a constantly decreasing value, since $\gamma_{Cl_2} \propto \frac{1}{S}$.

It would thus appear that the chlorine atom recombination mechanism, with or without diffusion and convection processes, cannot explain the present experimental results. Similar difficulties arise if the chain-ending processes involve CH_3 radicals. Further, the above schemes are not in agreement with the observed variation in concentration of reactants. Although, at low methane concentrations, the quantum efficiency is directly proportional to $[CH_4]$, the previous equations do not indicate any conditions where the quantum efficiency becomes independent of $[CH_4]$, as indicated experimentally. The methane molecule must be considered as playing the part of an M stabilising molecule: then at high $[CH_4]$, the quantum efficiency is proportional to $\sqrt{[CH_4]}$ in equation A, and would still be proportional to $[CH_4]$ in equation B. In this latter case, the increased convection would reduce the efficiency, but it seems improbable that the reduction would exactly compensate the expected increase due to linearity. In the same way, since Cl_2 will play the part of an M molecule, the quantum efficiency in equation A becomes inversely proportional to $\sqrt{[Cl_2]}$: the present results are not sufficient to decide this point exactly, but the results of Ritchie and Taylor[5] on the hydrogen-chlorine reaction, which show a distinct similarity to the present instance, indicate that the γ_{HCl} is inversely proportional to the first power of the chlorine concentration at high values of $[Cl_2]$. The results would come into line for both CH_4 and Cl_2, only if the convection effects were proportional to the square root of the concentrations of these gases. The results of Müller and Schumacher[61] on the photo-reaction between acetylene and bromine, show that at high pressures of added inert gases, the quantum efficiency becomes constant and independent of the nature of the added gas, the rate being proportional to I_{abs} and all the chain carriers being removed at the wall by convection.

In the present case, the addition of hydrogen chloride and nitrogen retards the rate to an approximately equal extent, and the index remains more or less unchanged. The retardation might be due to the effect of the $K_4[M]$ term in the denominator of equation A, and the fact that the rate index does not approach unity, due to increased convection, might be due to the compensating reduced diffusion, which would tend to produce "n" values, tending to 0.5.

In view of the various discrepancies and difficulties shown above, it appears unlikely that the previous mechanism can explain satisfactorily the results obtained.

We shall now consider the alternative mechanism involving the formation and removal of the intermediate Cl_3. This must also be taken as capable of removal by diffusion and convection processes: for simplicity, however, only the Cl atom removal by such means is, for the present, included.

A possible scheme is then:

$$Cl_2 \xrightarrow{h\nu} Cl + Cl \qquad k_1$$

$$Cl + CH_4 \longrightarrow CH_3 + HCl \qquad k_2$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl \qquad k_3$$

$$Cl + Cl_2 + M \longrightarrow Cl_3 + M \qquad k_4$$

$$Cl_3 + M \longrightarrow Cl + Cl_2 + M \qquad k_5$$

$Cl_3 + Cl_3 \rightarrow 3Cl_2$ — k

$$Cl \longrightarrow \tfrac{1}{2}Cl_2\text{, at wall} \qquad S$$

By the stationary state method, the quantum efficiency of chlorine molecule removal is:

$$\gamma_{Cl_2} = \frac{-\frac{d[Cl_2]}{dt}}{I_{abs}}$$

$$= \frac{k_2[CH_4]}{(k_4[Cl_2][M] + S)}\left(k_1 + \frac{k_1^{\frac{1}{2}}}{k_6^{\frac{1}{2}}}\,\frac{k_5[M]}{\sqrt{I_{abs}}}\right)$$

If I_{abs} is the only variable, as would be the case if S is determined solely by diffusion, the expression is of the form:

$$\gamma_{Cl_2} = a\left(b + \frac{1}{\sqrt{I_{abs}}}\right)$$

Calculation of quantum efficiencies from experimental results, using the above formula, when a = 2.48 and b = 0.75, gives the following results:

λ mu	$I_{abs} \times 10^{-12}$ quanta/sec.	$\gamma_{expt.}$	$\gamma_{calc.}$
365	78.7	2.14	2.14
365	44.8	2.24	2.23
365	7.6	2.34	2.76
365	4.0	2.90	3.10
406	2.77	3.52	3.35

This equation is then in agreement with experiment in that the quantum efficiency is approximately independent of I_{abs} at high values of I_{abs}, the value of the index n then approaching unity. At low values of I_{abs}, the quantum efficiency will become inversely proportional to $\sqrt{I_{abs}}$ and the index n will approach 0.5, again in agreement with experiment. This concordance thus suggests, for the present conditions of alteration in light intensity, that S is either constant or small enough in comparison with $K_4[Cl_2][M]$ to make negligible any variation in its magnitude. If convection were to play an appreciable part, the value of S would increase as I_{abs} (and the consequent rate of reaction) is increased, and the formula would then indicate a steadily decreasing value of the quantum efficiency. No pronounced tendency in this direction is to be observed experimentally,

As before, CH_4 and the other reactant and resultant molecules must be considered as playing the part of M molecules. At low values of $[CH_4]$ (HCl), M will remain approximately constant, and the quantum efficiency will be directly proportional to $[CH_4]$. For conditions where the quantum efficiency is independent of I_{abs} i.e. where I_{abs} is sufficiently high, so that the term is small in comparison with K_1, the formula indicates that such linearity with $[CH_4]$ will no longer exist, and at very high $[CH_4]$ values, since CH_4 plays the part of an M molecule, the quantum efficiency will tend to become independent of the CH_4 concentration. Indications of this have been observed experimentally (page 122). At the same time, since the $\frac{1}{\sqrt{I_{abs}}}$ term contains an M factor, this term will tend to increase, with a consequent lowering of the index. This was not investigated experimentally, because of the difficulty, attributed to minute traces of oxygen in the methane, of obtaining strictly reproducible results. It is under these conditions of very high methane pressures that convection effects will be at a maximum, with a corresponding lowering of the quantum efficiency. Again the effect of convection, as shown by increase in S, will tend to be minimised by the corresponding increase in $K_4[Cl_2][M]$.

In the same way, $K_4[Cl_2][M]$ will increase with addition of nitrogen or hydrogen chloride. No increase in quantum efficiency was observed for such additions, and it must therefore be concluded that any marked reduction in S, due to decreased diffusion, is absent.

The experimentally observed retardations by these gases is thus to be ascribed to the removal of Cl atoms by equation 4. In other stabilisations brought about by such additions of inert gas, the effect of hydrogen chloride is usually much greater than that of nitrogen, and to this extent, the similarity here in the retarding effects is unexpected. Also, the formula indicates an approach to index 0.5 as inert gas is added. Some slight indication of this is to be observed in the HCl observations at the higher HCl concentrations. That such a tendency does not continue may be due to increased convection, which, as already shown, tends to give an index value approaching unity.

There remains for consideration the effect of altered chlorine concentration. Since again, Cl_2 may play the part of an M molecule, a retardation by chlorine is to be expected. This was realised experimentally only at a relatively high chlorine pressure. It is difficult to discuss the effect of altered chlorine concentration on the rate of diffusion of Cl atoms to the wall, because of the relatively altered distribution of such atoms initially produced by light absorption. Certainly at low chlorine concentration, the value of S will rapidly increase, with a corresponding decrease in the overall quantum efficiency. At the same time, some other reaction removing chlorine atoms, may be in operation: introduction of the reverse of reaction 3 will, for example, introduce a term acting in the required direction.

It may be said in conclusion that this second scheme, involving Cl_3, does offer a possible explanation of the main features of this complicated reaction. There is a general similarity to the hydrogen-chlorine photo-combination, to which a Cl_3 mechanism can be applied.

Further experimental work will be necessary to obtain greater detail of the magnitudes of the various reactions: every care will be necessary with regard to the purity of the reactants: the extent of removal of chain intermediates by diffusion or convection will also require more investigation.

SUMMARY.

1. An attempt has been made to repeat and examine further a pressure effect previously reported by Ritchie and Smith:[8] namely, the increase in pressure to a temporary maximum when mixtures of chlorine and inert gas are illuminated, and the existence of a temporary minimum pressure when illumination ceases. Varying conditions of temperature, surface composition, size of vessel, inert gas, and light intensity have failed to confirm the existence of such effects, and accordingly, no support can be given for Ritchie and Smith's view that such pressure changes were due to the formation and adsorption of Cl_3 molecules.

2. Reaction between chlorine and toluene vapour has been observed to take place at 25°C, thermally and under the action of light. Both reactions occur to a considerable extent, and both are inhibited by oxygen. Quantum efficiency determinations in the presence of between 3.5 and 450 mm of oxygen have shown that its effect is rendered by an equation of the type

$$\gamma = \frac{a}{b + [O_2]}$$

analogous to the case of the hydrogen-chlorine photoreaction.

The thermal reaction obeys a 2nd order relationship, and the velocity constant under the given experimental conditions equals 8.2×10^{-23} mols.^{-1} secs^{-1}. It is considered that the equation

$$C_6H_5CH_3 + Cl_2 \longrightarrow C_6H_5CH_2Cl + HCl$$

represents the quantitative mechanism of the thermal reaction.

The presence of this thermal reaction only allows ~~in~~ an indirect measure of the quantum efficiency of the oxygen-free photo-reaction to be made. Taking into account the size of the corresponding oxygen-free thermal reaction, the quantum efficiency under detailed experimental conditions was calculated to be 7.4×10^4 molecules / quantum of light absorbed.

3. The photo-reaction between methane and chlorine has been observed under varying intensities of absorbed light, and at varying pressures of methane, chlorine, and the added gases, oxygen, HCl, and nitrogen.

The inhibitory effect of oxygen was found to be extreme.

A chain mechanism is undoubtedly present, and indirect evidence has been advanced, that it possesses the form

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$

$$Cl + CH_4 \longrightarrow CH_3 + HCl$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl$$

Two possible mechanisms have been examined in order to explain the various trends in the reaction, observed experimentally.

For oxygen-free mixtures, the quantum efficiency tends to approach inverse proportionality to the square root of the absorbed light intensity at low values of light intensity, but at high values, the quantum efficiency becomes independent of the absorbed light intensity: it is directly proportional to the methane concentration at low pressures of methane, but at high pressures, it approaches an approximately constant maximum. It is retarded equally by nitrogen and hydrogen chloride, and reaches a maximum at an intermediate pressure of chlorine.

With due consideration of diffusion and convection factors, it is regarded as possible that chains are brought to an end by the removal of chlorine atoms by formation of Cl_3 molecules.

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