STUDIES IN THE PHOTOCHEMISTRY OF CHLORINE

By

ROBERT L. SMITH, B.Sc.

Thesis submitted for the degree of
DOCTOR OF PHILOSOPHY

CONTENTS

GENERAL INTRODUCTION

PART I.

THE BUDIN EFFECT IN CHLORINE. ......................... 4
  1. HISTORICAL INTRODUCTION. ......................... 5
  2. DESCRIPTION OF APPARATUS. ....................... 12
  3. THEORETICAL DISCUSSION. ......................... 18
  4. EXPERIMENTAL PROCEDURE AND RESULTS ............ 41
  5. SUMMARY AND CONCLUSIONS. ....................... 67

PART 2.

THE THERMAL CONDUCTIVITY OF CERTAIN GASES AND GAS MIXTURES. .......... 70
  1. INTRODUCTION. .................................. 71
  2. DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE .......... 74
  3. RESULTS AND CALCULATIONS. ...................... 78
  4. CONCLUSIONS. .................................. 83

PART 3.

THE HYDROGEN-CHLORINE REACTION IN OXYGEN FREE MIXTURES .......... 84
  1. HISTORICAL INTRODUCTION. ......................... 85
  2. THEORETICAL DISCUSSION. ......................... 96
  3. DESCRIPTION OF APPARATUS ....................... 103
CONTENTS (CONTINUED).

4. EXPERIMENTAL PROCEDURE AND RESULTS. .......................... 107

5. DISCUSSION AND CONCLUSIONS. .................................... 126

GENERAL SUMMARY OF THE RESEARCH ................................. 140

TABLE OF REFERENCES .................................................. 146
THE AIM OF THE PRESENT RESEARCH.

The Budde effect in chlorine and the hydrogen-chlorine photocombination are two of the earliest observations in photochemistry, yet up till now their investigation has not been brought to a state of satisfactory completion. The Budde effect, the increase in pressure observed when chlorine is illuminated, is now recognised as due to the recombination of atoms initially produced by the photodissociation of the chlorine molecule; such recombination is an important factor in the mechanism of the hydrogen-chlorine reaction. Thus a complete study of the former paves the way to a better analysis of the latter. The mechanism of the combination of chlorine atoms is similarly of importance in many other reactions, and if, as has been suggested, a third otherwise inactive body is involved in it, all rates of reaction under similar conditions might be dependent on the pressure of added gas or of otherwise inert products of reaction.
THE SCOPE OF THE RESEARCH.

The Budde effect in chlorine was investigated with the addition of the following inert gases: -nitrogen, oxygen, argon, carbon dioxide and hydrogen-chloride. To establish whether or not slight traces of water vapour influence the magnitude of the Budde effect, experiments were also performed, both with the vessel baked out at 350°C together with evacuation by a mercury distillation pump, and with the intentional addition of small quantities of water vapour. The relation between the magnitude of the Budde Effect and the intensity of the light absorbed was studied by varying the illumination with a rotating sector.

As no value could be found in published work for the thermal conductivity of hydrogen-chloride, and as it was uncertain to what extent it was justifiable to calculate the thermal conductivities of mixtures of chlorine, with the above mentioned inert gases, as the sum of the partial values, actual measurement of relative values was carried out.

In the third part the information obtained about the mechanism of recombination of chlorine atoms was applied to the hydrogen-chlorine reaction.

Experiments/
Experiments were performed with light of wave-length 3650 A.U. The work of Ritchie and Norrish (1) suggests, as an essential part of the mechanism, that the rate of reaction would be proportional to the square root of the absorbed intensity if surface action could be eliminated. To this end a high intensity source of light was here used, and the time of reaction thereby reduced, for comparable concentrations of reactants, by a factor of ten as compared to the work referred to, to obtain a high concentration of chlorine atoms; it was hoped thus to obtain a rate proportional to the square root of the intensity. Measurements of the rate of reaction were made with mixtures in which the concentrations of chlorine, hydrogen and hydrogen-chloride were varied, together with variation of the intensity of the light in each case. The hydrogen-chloride used was prepared exclusively in the reaction vessel by the action of light with the normal hydrogen and chlorine supplies, thereby avoiding the criticism levied against the results of Ritchie and Norrish, that impurities might have been introduced into the system along with this gas.
PART I

THE BUDDE EFFECT IN CHLORINE
1. **HISTORICAL INTRODUCTION.**

The photo-expansion of chlorine, that is the increase in pressure ($\Delta p$) observed when chlorine is exposed to light, was discovered by Budde (2), after whom it has been termed the Budde effect. He showed that the phenomenon is due to some chemical change and not merely to the absorption of light. He also noticed that for constant light intensity the increase in pressure remains the same, and that the gas always returns to the original pressure when the light is shaded. Richardson (3) demonstrated conclusively that the effect was not a result of heat rays, and he believed that the increase in pressure was proportional to the intensity of the light. Baker (4) claimed that dry chlorine did not show the photo-expansion. Various workers have confirmed and contradicted this observation. A similar state of disagreement existed till lately for bromine, but it was shown by W. Smith, Ritchie, and Ludlam (5), and is now generally accepted, that the removal of the last trace of water vapour, both from the bromine gas, and from the walls of the reaction vessel, does not appreciably decrease the effect for bromine, and it has been concluded, that the apparent non-existence of the Budde Effect in perfectly dry bromine, reported by many workers, was due/
due to the introduction of inhibitors in the process of drying. It was shown by Martin, Cole and Lent (6), and by Kistiaakowsky (7), that the careful drying of chlorine does not prevent the photoexpansion, a conclusion which is confirmed in this work. The mechanism, which will be shown to offer a consistent explanation of the results, does not admit of the necessity of water vapour; while in those experiments in which traces of water vapour have been intentionally added, it will be found that its effect is small and due only to a modification of the surface of the reaction vessel.

Mellor (8), by means of an ingenious gas thermometer apparatus, showed that the photoexpansion is a thermal effect, the heat being liberated in a secondary process.

The primary process of the dissociation of chlorine molecules, should, according to the general principles worked out by Franck (9) and others take place in the form:

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}^* \]

where \( \text{Cl}^* \) is an excited atom. This was verified experimentally by Turner (10), who showed that the heat of dissociation of the chlorine molecule is 56.9 kilogram calories (spectroscopic), while the excitation energy of the excited chlorine atom is 2.5
2.5 kilogram calories. It may be pointed out here that if the light quantum absorbed is just sufficient to dissociate the molecule into a normal and an excited atom (light of the wavelength corresponding to the convergence limit), then the kinetic energy of the resultant atoms can be taken as the same as that of the original molecule, and any change in pressure on dissociation will be due to the energy of excitation of the excited atom transferred in collision. This effect will be smaller if the wavelength employed is greater than that of the convergence limit, in which case dissociation will occur only after collision of an excited molecule with another body. If the quantum be of greater energy than that required for dissociation, the excess energy will appear as kinetic energy of the products with a consequent increase in temperature. The nature of the light absorbed is considered later, but it may be said here that the importance of these factors is small under the conditions of experiment compared with the heat produced in the subsequent recombination of the chlorine atoms. If all the chlorine atoms recombine in the gas phase the heat so produced will of course be equivalent to the energy absorbed from the light beam.

It is now necessary to make a short historical/
historical survey of some aspects of the hydrogen-chlorine reaction in oxygen-free mixtures, where the recombination of chlorine atoms has been considered as a chain-breaking mechanism. Only points relevant to the mechanism of recombination will be dealt with now, and the more complete discussion of this reaction will be left to Part 3 of this thesis.

The earliest papers of Bodenstein and his co-workers did not envisage the recombination of chlorine atoms in the gaseous phase, and even his mechanism of reaction in 1916 (11) did not introduce any chlorine atoms at all. Nernst (12), in his chain reaction scheme involving the primary dissociation of chlorine molecules, introduced the equation

\[ \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \]

as a chain-breaking mechanism. The possibility of the formation of \( \text{Cl}_3 \) molecules during the reaction was first suggested by Gohring (13), who introduced the reaction

\[ \text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_3 \]

but neglected all reactions involving the \( \text{Cl}_3 \) molecule in his kinetic expression as unimportant. Thon (14) introduced the \( \text{Cl}_3 \) molecule into his scheme of reaction, as did also Cremer (15).

In 1925 Born and Franck (16), from quantum mechanical/
mechanical considerations, concluded that the formation of a homopolar diatomic molecule required a triple collision of two atoms and a third body acting as a stabilizer. Thus a simple reaction of the type

$$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$$

was not to be expected, while if the original conclusions of Born and Franck were correct a reaction of the form

$$\text{Cl} + \text{Cl} + M \rightarrow \text{Cl}_2 + M$$

would be required. In the case of bromine this mechanism has been proved correct by Rabinowitch and Wood (17) and confirmed by W. Smith, Ludlam and Ritchie (loc. cit.). In 1932 Rollefson and Eyring (18) from quantum mechanical equations for the potential energy of systems of three atoms, showed that for all halogens the molecules of the type $X_3$ were relatively stable at room temperature with respect to decomposition into $X_2$ and $X$. The formation of $\text{Cl}_3$ was put forward as a two body mechanism:

$$\text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_3$$

without the necessity for a third body as stabilizer.

Craggs and Allmand (19) assumed the formation of $\text{Cl}_3$ molecules in their investigation of the hydrogen-chlorine reaction. They found it necessary to assume under certain conditions a higher ratio for $(\text{Cl}_3)/(\text{Cl})$ than that corresponding to the equilibrium:
equilibrium:–

\[ \text{Cl} + \text{Cl}_2 \rightleftharpoons \text{Cl}_3 \]

They also suggested that Cl\(_3\) molecules are more readily adsorbed on the walls than are Cl atoms. In a later paper Craggs, Squire and Allmand (20) in considering the removal of Cl\(_3\) molecules suggested:

1. \[ \text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl} \]
2. \[ 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \]
3. \[ \text{Cl} + \text{Cl}_3 \rightarrow 2\text{Cl}_2 \]

but concluded that only 2 was significant though at very low pressures of chlorine 3 might play an increasing part. Craggs and Allmand (21) further suggested the possibility of the triple collision:

\[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \]

as a recombination mechanism, but no definite experimental evidence seems available. As already pointed out the question is of importance in view of the fact that all rates of reaction involving chlorine atoms, under similar conditions, would then be dependent on the pressure of added gas or otherwise inert products of reaction. Ritchie and Norrish (loc. cit.) gave data to show that in oxygen-free mixtures of hydrogen and chlorine the rate of photocombination was retarded by hydrogen-chloride itself, and this apparent effect has been the object of considerable investigation and discussion/
discussion (inter alios; Craggs, Squire and Allmand (loc. cit.); Potts and Rollefson (32). Recent investigation has favoured the view that any possible effect of hydrogen-chloride is connected with surface action only. Since the analysis of the Budde Effect in bromine involved consideration of surface effects, as well as the kinetics of atomic recombination in the gas phase, a similar examination of the Budde Effect in chlorine was thought likely to be most effective in settling the matter.
2. DESCRIPTION OF APPARATUS.

The apparatus is shown diagramatically in Figure 1. The reaction vessel was a spherical bulb of soft glass of capacity about 1500 c.c., immersed in water thermostatically controlled by a circulating water system. The source of illumination was a 200 watt Osira mercury vapour lamp run at 220 volts, the voltage being controlled by means of a Solus stabilizer, which reduced variations in voltage to \( \pm 1\% \). The light passed through a 5\% solution of copper sulphate contained in a 500 c.c. flask, which acted as a focussing lens as well as a light filter. The light emerging from the reaction vessel was re-focussed by a similar flask of distilled water on to a photronic cell, enclosed in a wooden box with black matt interior and small circular aperture. The current from the cell was recorded by a mirror galvanometer, the light absorbed being measured as the difference of galvanometer readings.

Figure 1.
Cylinder chlorine was passed through two wash bottles containing alkaline potassium permanganate and one containing concentrated sulphuric acid. It was then passed through a tube of phosphorus pentoxide, and fractionated several times by means of liquid air between the traps T₁ and T₂, and was kept in the solid state in T₂ surrounded by liquid air. Nitrogen, oxygen and argon, obtained from cylinders, were passed through phosphorus pentoxide and the liquid air trap T₅ before storing in the flasks F₁ and F₂. Carbon dioxide was obtained both from cylinders and from the action of dilute hydrochloric acid on calcium carbonate, and was purified by successive treatment with sodium carbonate, concentrated sulphuric acid, phosphorus pentoxide and a carbon dioxide - ether mixture. Hydrochloric acid was prepared both by the action of concentrated sulphuric acid on concentrated hydrochloric acid and by photosynthesis within the apparatus as will be subsequently described. The hydrogen-chloride from the concentrated acid was dried with phosphorus pentoxide and fractionated by liquid air traps.

The pressure in the inert gas line was measured by the manometer M₂, which was closed when desirable by the tap t₁₉. Hydrogen was prepared by electrolysing an aqueous solution of potassium hydroxide and baryta, and was collected temporarily in a reservoir/
reservoir over distilled water saturated with the
gas (not shown in diagram), before passing through
a catalyst tube containing copper foil maintained at
350°C by a heating coil covered with asbestos windings,
and then over a tungsten filament at dull red heat.
The gas was passed over phosphorus pentoxide and then
stored in the flask $F_3$. For the experiments with
water vapour, a sealed tube with ground glass tap $t_{25}$
was filled with distilled water, freed from residual
gas by boiling at reduced pressure at room temperature.
The tube was connected at the main inert gas line. It
was attached only just before it was required and
was drawn off immediately it was no longer necessary.

The high vacuum line led from the Myvac
oil pump through the tap $t_1$ to a phosphorus pentoxide
tube. During those experiments connected with the
study of a baked-out reaction vessel a mercury pump
system was fitted in here, consisting of a mercury
distillation pump with taps $t_{27}$ and $t_{28}$ at either
side, and also a direct by-pass through tap $t_{29}$ for
use in evacuating large quantities of gases, especially
chlorine, until a small residual pressure only
remained. Thence the high vacuum line passed
through a liquid air trap used to prevent chlorine
reaching the pump. After passing through the tap
$t_2$ there were two junctions. The first led through
the tap $t_3$ to the low vacuum line, while the second
through/
second through the tap $t_7$ led to the reaction vessel and the Bourdon Gauge. Another junction further down the line passed through the tap $t_8$ to divide into three lines; one to the outer surface of the Bourdon gauge, the second to the mercury manometer $M_1$ through tap $t_{10}$, and the third to the two-way tap $t_9$. One line from $t_9$ opened to the air through a tube containing anhydrous calcium chloride and phosphorus pentoxide to remove impurities. Air was admitted in this way to the manometer $M_1$ and to the outer part of the gauge. The other arm led to the low vacuum line. Beside the manometer $M_1$ was on the one side a second manometer $M_3$ closed by the tap $t_{11}$ to register the vacuum obtainable by the pump, and on the other a barometer tube to indicate atmospheric pressure.

The low vacuum line passed to the water pump through the tap $t_5$, a T junction with tap $t_6$ being inserted so that the vacuum at the pump could be relieved before turning off the water. For convenience in fractionating chlorine, the low vacuum line led through the taps $t_{15}$ and $t_{13}$ to either side of the tap $t_{14}$ separating the liquid air traps $T_1$ and $T_2$.

The temperature of the reaction vessel and Bourdon gauge was kept constant at $25^\circ C$ by means of a circulating/
circulating water system. Water from a thermostat tank was pumped to a constant level reservoir above the apparatus, whence it descended through a glass wool filter, which was renewed every day; one branch passed through the jacket of the Bourdon gauge, while the other lead to the base of the water bath surrounding the reaction vessel. The overflows returned to the thermostat tank.

The pressure of gas in the reaction vessel was measured by slightly opening both the taps \( t_7 \) and \( t_9 \) simultaneously when admitting gas and regulating the inflows so that the pressure difference indicated by the pointer of the Bourdon gauge remained zero. The pressure of gas in the reaction vessel at any moment was that registered by the manometer \( M_\perp \). Before commencing any experiment the reaction vessel was first washed out with chlorine.

Where photosynthesised hydrogen-chloride was used as the inert gas, the volume of chlorine equivalent to both the chlorine and the hydrogen-chloride required was first admitted, and then the hydrogen equivalent to the hydrogen-chloride was added. The vessel was illuminated with slowly increasing intensity of light, and was finally given at least an hour's full illumination after the reaction was apparently complete.

The/
The mercury vapour lamp was enclosed in a wooden box with circular aperture in front of which was a holder in which a monochromatic glass plate could be fitted. In front of this was a sliding copper foil shutter on a rod, which could be moved to and fro to obscure the light when required. For experiments with light of varied intensity a rotating sector was inserted between the lamp and the focussing lens.
3. THEORETICAL DISCUSSION.

Before quoting the main results and discussing the possible mechanisms of the recombination of chlorine atoms, it is convenient to mention a series of observations which were not observed in the corresponding experiments on the Budde effect in bromine by W. Smith, Ritchie and Ludlam (loc. cit.). These form such a marked indication of the possible mechanism that it is essential to discuss them when reviewing the latter, and therefore they cannot be given later with the other experimental results. In certain mixtures the initial illumination, instead of causing a direct rise of pressure to a steady value, produced an increase to a maximum which was not maintained, a slightly smaller value being finally reached. Similarly, when the light was cut off, the pressure as shown by the pointer of the Bourdon gauge decreased to a minimum less than the initial pressure of the mixture, but then increased and regained this value exactly. Figure 2 and Table 1 show the increase of pressure with time of illumination for a particular gas mixture. Accurate determination of the value was difficult in view of the smallness of the effect, but Figure 3 and Table 2 show the mean differences from several series of observations for 50 m.m. of chlorine with/
with varying pressures of nitrogen. The effect was found to have the same values within the possible accuracy of measurement for nitrogen, oxygen and argon. It was not observed in the case of carbon dioxide or of hydrogen chloride.

**Table 1.**

Movement of the gauge pointer with time of illumination

<table>
<thead>
<tr>
<th>TIME (secs.)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light on</td>
<td>47.0</td>
<td>51.0</td>
<td>53.0</td>
<td>53.6</td>
<td>53.8</td>
<td>53.7</td>
<td>53.5</td>
<td>53.2</td>
<td>53.1</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>Light off</td>
<td>53.0</td>
<td>49.0</td>
<td>46.0</td>
<td>47.0</td>
<td>46.4</td>
<td>46.2</td>
<td>46.4</td>
<td>46.8</td>
<td>47.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.**

**Movement of gauge pointer with time of illumination.**

50 m.m. $\text{Cl}_2 + 300 \text{m.m.} \text{O}_2$.
TABLE 2

PRESSURE OF ADDED GAS (mm.)
0 100 200 300 400 500 6000

MAGNITUDE OF EFFECT (divisions of telescope scale)
0 0.2 0.4 0.8 0.5 0.2 0

Figure 3

MAGNITUDE OF THE "SURFACE EFFECT"
WITH VARIED PRESSURE OF ADDED GAS.

50 m.m. CL₂
WITH OXYGEN, NITROGEN AND ARGON.
Data are also given for the time to attain the minimum and equilibrium readings of the gauge pointer when the light is masked for 50 mm. chlorine with varying pressures of oxygen. Very similar results were obtained on exposing the vessel to the light.

**TABLE 3**

<table>
<thead>
<tr>
<th>PRESSURE OF OXYGEN (mm.)</th>
<th>0</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIME TO EQUILIBRIUM (seconds)</td>
<td>13</td>
<td>25</td>
<td>45</td>
<td>60</td>
<td>90</td>
<td>120</td>
<td>180</td>
</tr>
<tr>
<td>TIME TO MAX. DEFLECTION (seconds)</td>
<td>13</td>
<td>15</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>100</td>
<td>180</td>
</tr>
</tbody>
</table>

Figure 4.
The value of the pressure difference of the abnormal effect is the same both on illuminating and shading the reaction vessel. The maximum when the vessel is illuminated appears to be attained more rapidly than the minimum when it is shaded. The final equilibrium value is attained in about the same time in each case.

The effect, when the vessel is illuminated, might be attributed to an excess of heat energy in the gas before thermal conductivity equilibrium is completely established, the time value being in general agreement with this hypothesis. A similar explanation cannot hold however for the decrease observed on cutting off the illumination. It is unlikely therefore that the cause is connected with a rise or fall in temperature of the main body of the gas. Some species must be produced as a result of illumination, which is adsorbed to some extent on the walls of the vessel. This species is completely desorbed into the main body of the gas when its equilibrium concentration is no longer maintained by continued adsorption after the light is cut off. The pressure increase ($\Delta p$) of the steady state is less than the value which would be recorded if no such adsorption occurred. Correspondingly when the light is cut off the pressure falls to less than/
than the original value, and only returns to the initial pressure when the adsorbed product escapes into the gas phase. The effect is negligible at zero pressure of added gas; adsorption of chlorine atoms is thus not regarded as responsible, since the number of atoms then reaching the wall would be at its maximum. It is therefore due to a species which becomes increasingly important as the inert gas added prevents chlorine atoms reaching the walls by diffusion. At the highest pressures employed the species is regarded as prevented from reaching the wall by the inert gas. It does not accumulate, but is removed in the gas phase. The effect at 600 mm. of inert gas is substantially zero. Such observations indicate that the process occurring in illuminated chlorine is essentially different from that in illuminated bromine.

If a Cl₃ molecule is formed in the process of recombination of chlorine atoms it could play the part visualised above for an adsorbed species and explain this abnormality in the Budde effect. It is necessary from the above observations that the species Cl₃ should be formed by a three body collision since otherwise the effect would at a maximum at low pressure of added gas, and would progressively decrease with each addition. If formed by a three body collision however/
however, the effect will increase until the added gas finally prevents the \( \text{Cl}_3 \), though increasingly formed, from reaching the wall in as great a number. This agrees with the observations. This effect thus indicates that any true mechanism of recombination should include a species such as a \( \text{Cl}_3 \) molecule, which, in addition, is formed by a triple collision.

In view of the above adsorption effect the true Budde effect is not the difference between the original dark pressure and the pressure in the steady state of illumination, but rather the change in pressure which would have been observed if no adsorption had occurred. The maximum pressure difference observed was therefore taken as the Budde effect. This value will be somewhat less than the true increase, as adsorption or desorption must be taking place even in the short time taken for this difference to reach its maximum value. The error thus introduced is regarded as small since the adsorption effect AB of figure 2 is, at its maximum, about 10% of the total change. An examination of the slope of the curves of figure 2 after the maximum and the minimum suggests also that comparatively little adsorption and desorption occurs before the attainment of the maximum difference, as the initial gradient after this point is small and subsequently increases/
increases before finally tailing off.

The absence of the effect in the case of hydrogen-chloride and carbon dioxide is perhaps not unexpected. Physical adsorption at a surface occurs readily with substances whose boiling point lies not greatly below the temperature of the experiment, and with increasing difficulty as this interval increases. The "permanent" gases such as oxygen, nitrogen and argon are thus very sparingly adsorbed and will not hinder the adsorption of the Cl₂ molecule, while carbon dioxide and hydrogen-chloride will be relatively easily adsorbed, and will entirely change the nature of the wall.

Budde effects (Δp) are given in the results as divisions of the telescope scale, with an approximate error of ± 0.1 divisions (1 division = 0.0476 mm.).

In the examination of each mechanism of reaction, chlorine atoms are taken to be formed as the direct result of the absorption of the light of the wavelengths transmitted by the system. The nature of the light absorbed by the chlorine will depend on the absorption spectrum of chlorine, the absorption of light by the glass bulb and focusing flask, and the spectrum of the mercury arc. Consider the glass first as this is the chief limiting factor. The extinction coefficient of soda glass (23) is given in table 4.
TABLE 4.

Extinction coefficient ($\varepsilon$) of soda glass.

<table>
<thead>
<tr>
<th>WAVELENGTH (A.U.)</th>
<th>EXTINCTION COEFFICIENT $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3150</td>
<td>7.6</td>
</tr>
<tr>
<td>3200</td>
<td>5.0</td>
</tr>
<tr>
<td>3400</td>
<td>1.29</td>
</tr>
<tr>
<td>3600</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$\varepsilon$ is defined by $I = I_o e^{-\varepsilon d}$ where $d$ is the thickness in cms. From this table it appears that all the lines of the mercury spectrum of wavelength less than 3400 A.U. may be neglected. The copper sulphate filter solution will cut all lines in the red and orange and hence we may neglect lines beyond 5800 A.U.

The absorption of light by a gas at various wavelengths is commonly expressed as the extinction coefficient defined by the equation $I = I_o 10^{-\alpha d}$ where $\alpha$ is the decadic extinction coefficient, $I$ and $I_o$ are the intensities of the transmitted and incident light respectively and $d$ is the thickness of the absorbing layer. Values for chlorine have been given by many workers(84) and Figure 5 is drawn from accepted results.
The absorption curve shows a maximum at about 3340 A.U. and a minimum in the yellow. From the yellow the absorption increases and reaches a second maximum between 6140 and 6430 A.U., but as already stated a second portion is cut out by the filter solution. From the graph it is evident that no appreciable absorption will take place beyond 4500 A.U.

It is therefore only necessary to consider that portion of the mercury arc spectrum lying between 3400 and 4500 A.U. The exact output in quanta for the various lines of the mercury spectrum varies with different/
different lamps, but the following values of A.J. Maddock (25) give an indication of the relative values.

TABLE 5.

Output at different wavelengths of a mercury vapour lamp.

<table>
<thead>
<tr>
<th>Wavelength in A.U.</th>
<th>Output in quanta per sec. per sq. cm. at 100 cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4358, 4329</td>
<td>1.89 x 10^{14}</td>
</tr>
<tr>
<td>4078, 4047, 3984</td>
<td>9.5 x 10^{13}</td>
</tr>
<tr>
<td>3906</td>
<td>2.6 x 10^{12}</td>
</tr>
<tr>
<td>3704, 3663, 3655, 3650</td>
<td>2.5 x 10^{14}</td>
</tr>
</tbody>
</table>

For simplicity take the groups of lines at the approximate mean values conventionally given them. We then have four lines 4360, 4050, 3906 and 3660 A.U. with relative intensities 1.89, 0.95, 0.026 and 2.5. By reference to the graph of extinction coefficients for chlorine we get the following approximate corresponding values of $\alpha$: -0.12, 0.35, 0.6 and 1.5, which lead to values for $l\cdot l_0$ and $d$ being taken as unity, of 0.7586, 0.4476, 0.2512, and 0.03162. Hence $l_0 - l = 0.2414, 0.5555, 0.7438$ and 0.9684 respectively. But the true $I_{abs}$ is output $x (l_0 - l)$, the values of which are given below in Table 6.
TABLE 6.

Intensities of the wavelengths of light absorbed by chlorine.

<table>
<thead>
<tr>
<th>WAVELENGTHS</th>
<th>4360</th>
<th>4050</th>
<th>3906</th>
<th>3660</th>
</tr>
</thead>
<tbody>
<tr>
<td>RELATIVE OUTPUT</td>
<td>1.89</td>
<td>0.95</td>
<td>0.026</td>
<td>2.5</td>
</tr>
<tr>
<td>((l_0 - l))</td>
<td>0.2414</td>
<td>0.5535</td>
<td>0.7488</td>
<td>0.9684</td>
</tr>
<tr>
<td>(I_{ab})</td>
<td>0.456</td>
<td>0.525</td>
<td>0.195</td>
<td>0.242</td>
</tr>
</tbody>
</table>

The absorption of light at 3906 A.U. is evidently insignificant, and the effective absorption may be considered as consisting approximately of 2/5 of the intensity at each of 4360 and 4050 A.U., and 1/5 at 3660 A.U. These figures take no account of the exact absorption of light by glass where the bulk is transmitted.

The convergence limit of chlorine is 4785 A.U. (59.4 K. cals) and the energy of dissociation 56.9 K. cals. while the proportional mean of the wavelengths of the 3 lines effectively absorbed is 4100 A.U. (69.4 K. cals.).

Mechanism I.

The examination of the Budde Effect in bromine/
bromine by W. Smith, Ritchie and Ludlam (loc. cit.) established the mechanism:

1. \( \text{Br}_2 \xrightarrow{h\nu} \text{Br} + \text{Br} \)
2. \( \text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} \)
3. \( \text{Br} + \text{wall} \rightarrow \frac{1}{2}\text{Br}_2 \)

The concentration of atoms in the gas phase is reduced by removal of atoms by the walls of the reaction vessel. At higher pressures of bromine this effect decreases. The addition of inert gas will hinder atoms diffusing and where as in this case the reaction is a three body mechanism it will still further increase the preponderance of recombination in the gas phase by increasing the concentration of third bodies.

If the reaction in chlorine is of the same form as that for bromine, then the mechanism becomes:

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Velocity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{Cl}_2 \xrightarrow{h\nu} \text{Cl} + \text{Cl} )</td>
<td>( k_1 )</td>
</tr>
<tr>
<td>2.</td>
<td>( \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} )</td>
<td>( k_M )</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{Cl} + \text{wall} \rightarrow \frac{1}{2}\text{Cl}_2 )</td>
<td>( S )</td>
</tr>
</tbody>
</table>

\( S \) \([\text{Cl}]\) is the rate of removal of atoms from the gas phase to the wall, and includes the rate of diffusion to the wall through the gas mixture as well as the collision factor depending on the nature of the wall itself. With a large reaction vessel and a high concentration/
concentration of reactants reaction 2 will predominate over reaction 3. The total heat evolved in the gas phase is then proportional to $I_{abs}$. At equilibrium the increase of temperature is dependent on the rate of conduction of heat to the thermostated walls, and hence on the thermal conductivity of the gas mixture.

In the photostationary state:

$$\frac{d [Cl]}{dt} = k_{1} I_{abs} - k_{M} [Cl][M] - S[Cl] = 0$$

(1)

Any rise in temperature in the gas phase results from reaction 2 and any heat evolved in reaction 3 is lost on the walls. Hence the heat produced in the gas phase is proportional to $k_{M}[Cl][M]$. In the steady state, the rate at which heat is transferred to the walls will be equal to the rate of heat evolution in the gas phase, and the rise in temperature will be dependent on the thermal conductivity of the gas mixture.

The beam of light used in the experiments was relatively narrow, fixed in position, and traversed a gas mixture between thermostated walls. We can use the general conductivity formula:

$$Q = K \cdot A \cdot \Delta T / x$$

where $Q$ is the heat quantity transferred per second across an area $A$, $\Delta T$ is the difference in temperature between two planes at a distance $x$, and $K$ is the thermal conductivity coefficient of the medium between the/
the two planes, in the form:

\[ Q \propto \Delta T \cdot K. \]

where \( \Delta T \) represents the rise in temperature of the mixture in the illuminated steady state. The increase in pressure in a gas mixture is proportional to the rise in temperature. Therefore

\[ Q \propto \Delta p \cdot K. \]

and \[ Q \propto k_M [Cl]^2 [M] \]

Hence \[ K \Delta p \propto k_M [Cl]^2 [M] \]
or \[ R K \Delta p = k_M [Cl]^2 [M] \]

where \( R \) is a constant.

From equation (1)

\[ [Cl] = \left( -3 + \sqrt{S^2 + 4k_1 I_{abs} k_M [M]} \right) / 2[M] k_M \]

\( k_1 \) may be taken as 2, and \([Cl]\) must be positive.

Therefore

\[ [Cl] = \left( -3 + \sqrt{S^2 + 8 I_{abs} k_M [M]} \right) / 2[M] k_M \]

But \[ R K \Delta p = k_M [M][Cl] = 2 I_{abs} - S[Cl] \]

Hence, substituting for \([Cl]\)

\[ R K \Delta p = 2 I_{abs} - S \left( \sqrt{S^2 + 8 I_{abs} k_M [M]} - S \right) / 2k_M = \]

\[ \frac{[Cl_2]}{2} k_{Cl_2} + [X] k_X \]

For mixtures of chlorine and one inert gas \([M]\) \( k_M \) must be replaced by \( k_{Cl} + [X] k_{X} \), where \( X \) is the pressure of the inert gas. Equation 2 then becomes

\[ R K \Delta p = 2 I_{abs} - S \left( \frac{S^2 + 8 I_{abs} [Cl_2] k_{Cl_2} + [X] k_{X} - S}{2([Cl_2] k_{Cl_2} + [X] k_{X})} \right) \]

or \[ R K \Delta p = 2 I_{abs} - Y \]

whence

\[ I_{abs} = \frac{1}{2} (R K \Delta p + Y) \]
The thermal conductivity $K$ will differ for each gas mixture. Actual measurements of these were made in Part 2 of this research.

Where a species diffuses through a mixture of gases whose diffusion coefficients are $D_1$, $D_2$ etc. respectively, the time required to diffuse a given distance is proportional to the sum of the reciprocals of these coefficients.

$$t \propto \left( \frac{1}{D_1} + \frac{1}{D_2} + \ldots \right)$$

Now $S$ the rate at which chlorine atoms reach the walls of the vessel and are removed is inversely proportional to $t$, hence

$$S = m \left( \frac{1}{D_1} + \frac{1}{D_2} + \ldots \right)^{-1}$$

where $m$ is a constant depending on the vessel dimensions, nature of the wall etc. and

$$D \propto \frac{1}{X \left( \frac{1}{MA} + \frac{1}{MX} \right)^{1/2}}$$

Here $MA$ is the molecular weight of the particle diffusing i.e. the chlorine atom. $MX$ is the molecular weight of the inert gas $X$. $[X]$ is the pressure of the inert gas and $\bar{r}_{AX}$ is the sum of the radii of the inert gas molecule and atom. Possible convection effects are neglected as being of small importance, while the possible increase in pressure due to the dissociation itself has already been discussed and found/
found negligible.

The full analysis of the results will be delayed till later but certain indications may now be given briefly. The formula

\[ I_{\text{abs}} = \frac{1}{2} (R K \Delta p + Y) \]

can be tested by reference to the variation of \( \Delta p \) due to \( I_{\text{abs}} \); for a given mixture all other factors remain constant. If the above mechanism is the correct one the observed \( \Delta p \) will not be directly proportional to \( I_{\text{abs}} \).

The sensitivity of the photronic cell varied with the wavelength and therefore the use of filter solutions or glass plates to alter the intensity could not conveniently be employed. The rotating sector method was accordingly adopted to give a reduced intensity of half the initial value; a greater reduction gave values of \( \Delta p \) too small for accurate measurement. As will be found in the results later \( \Delta p \) is proportional to \( I_{\text{abs}} \) within the limits of experimental accuracy over the entire region from zero pressure of inert gas to 500 mm. Further, the adsorption effect described above cannot be explained on the basis of this mechanism. The demonstration of the impossibility of fitting the general Budde effect results to equation 3 will be given under calculation of results.

**Mechanism 2.**

The second mechanism which will be considered
is based on the work of Rollefson and Eyring (loc. cit.) who suggested from quantum considerations:

\[
\text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_3
\]

\[
\text{Cl}_3 + \text{Cl}_3 \rightarrow 3\text{Cl}_2
\]

no third body being held to be necessary as a stabilizer. This leads to the full mechanism:

\[
\begin{align*}
\text{Cl}_2 & \xrightleftharpoons[k_1]{h\nu} \text{Cl} + \text{Cl} \\
\text{Cl} + \text{Cl}_2 & \rightarrow \text{Cl}_3 & k_2 \\
\text{Cl}_3 + \text{Cl}_3 & \rightarrow 3\text{Cl}_2 & k_3 \\
\text{Cl} & \rightarrow \frac{1}{2}\text{Cl}_2 \text{ at surface} & S \\
\text{Cl}_3 & \rightarrow \frac{3}{2}\text{Cl}_2 \text{ at surface} & S_1
\end{align*}
\]

The rise in pressure on illumination will be due to the heat liberated in reactions 2 and 3. Adsorption of chlorine atoms and \( \text{Cl}_3 \) molecules on the wall will reduce the heat effect, and hence the diffusion of both species to the walls should be considered. It does not follow that such adsorptions will occur at every collision with the wall, and Craggs, Squire and Allmand (loc. cit.) have indicated that different surfaces may have different efficiencies of adsorption of \( \text{Cl} \) and \( \text{Cl}_3 \). The \( \text{Cl}_3 \) molecule by virtue of its size and weight will diffuse much more slowly; the difficulties of calculation of the effective diffusion of both \( \text{Cl} \) and \( \text{Cl}_3 \) are such that the assumption has been/
been made that the adsorption of Cl₃ is not appreciable. This, of course, will not be exactly correct as indicated by the "abnormal effect" above mentioned, but in view of the smallness of this effect the broad conclusions drawn are regarded as justifiable. Furthermore, the adsorption effect indicates a high degree of stability in the Cl₃ molecule when adsorbed on the surface of the vessel, since, for instance, at 400 mm. inert gas a measurable concentration is present 60 seconds after the light is cut off.

If the Cl₃ molecules formed are then converted in the gas phase to Cl₂ molecules, the heat produced in the gas phase is proportional to [Cl] [Cl₂], and in the steady state will be equal to the heat transferred to the walls per second. The rise in temperature will depend on the thermal conductivity of the gas mixture. As was stated under the previous mechanism the general conductivity formula may be applied in the simpler form \( Q \propto K \Delta T \).

For any gas mixture the increase in pressure is proportional to the rise in temperature; hence

\[ Q \propto K \Delta P \]

and

\[ K \Delta P \propto [Cl] [Cl₂] \]

In the photostationary state, by mechanism 2

\[
\frac{d[Cl]}{dt} = k_1 I_{abs} - k_2 [Cl] [Cl₂] - s [Cl] = 0
\]

where/
where \( S \) is the factor representing the rate of diffusion of \( Cl \) atoms to the wall.

Hence 
\[
[Cl] = \frac{k_1 I_{abs}}{(S + k_2 [Cl_2])}
\]

and
\[
K \Delta p \propto \frac{[Cl_2] k_1 I_{abs}}{(S + k_2 [Cl_2])}
\]

This expression meets the requirement that \( \Delta p \propto I_{abs} \).

It may be further noted that if an appreciable number of \( Cl_3 \) molecules should be adsorbed on the walls and destroyed, the competition between this process and the bimolecular recombination to \( Cl_2 \) molecules would yield an \( I_{abs} \) term in the expression for \( \Delta p \) contrary to experiment.

If we consider equation 2 as reversible by introducing
\[
Cl_3 \rightarrow Cl_2 + Cl
\]
with the coefficient \( k_4 \), the heat produced in the gas phase then involves three terms: \( k_2 [Cl] [Cl_2] \), \( k_4 [Cl_3] \), and \( k_3 [Cl_3]^2 \). Since as much heat must be absorbed in the reverse action as is liberated in the forward action
\[
Q = k_2' (k_2 [Cl] [Cl_2] - k_4 [Cl_3]) + k_3' k_3 [Cl_3]^2
\]
where \( k_2' \) and \( k_3' \) take account of the fact that different amounts of heat are involved in the two stages. For equilibrium conditions represented by the reversible equation
\[
Cl + Cl_2 \rightleftharpoons Cl_3
\]
the equilibrium constant \( k = \frac{[\text{Cl}][\text{Cl}_2]}{[\text{Cl}_3]} \), and application of the previous method gives

\[
Q \propto I_{\text{abs}} \frac{[\text{Cl}_2]}{(s + (k_2 - k_3/k) [\text{Cl}_2])}
\]

which is of the same general type as before. No distinction thus appears between the two mechanisms. If the \( \text{Cl}_3 \) equilibrium is not attained, the analysis is more complicated and yields terms in \( I_{\text{abs}}^\frac{1}{2} \).

As was shown earlier, the variation of the surface effect with inert gas pressure indicates, not merely the formation of the \( \text{Cl}_3 \) molecule, but also that this process is brought about by the action of third bodies, which is contrary to this mechanism. The testing of this formula with regard to variation of \([\text{Cl}_2]\) cannot be conveniently examined, because increase of chlorine pressure causes the position of maximum absorption to move nearer to the wall where the light enters, thus altering the position of the source of Cl atoms and increasing the difficulty of calculation of the diffusion factors for the various pressures. It can however be tested in relation to \( S \) by the addition of other gases.

**Mechanism 3.**

Craggs, Squire and Allmand (loc. cit.) suggested the possibility of the triple collision:

\[
\text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M}
\]

which/
which leads to the mechanism:

1. \[ \text{Cl}_2 + \lambda \rightarrow \text{Cl} + \text{Cl} \]
2. \[ \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_3 + M \]
3. \[ \text{Cl}_3 + \text{Cl}_2 \rightarrow 3\text{Cl}_2 \]
4. \[ \text{Cl} \rightarrow \frac{1}{2} \text{Cl}_2 \text{ at surface } S \]

In this case the heat produced in the gas phase is proportional to:

\[ [\text{Cl}] [\text{Cl}_2] [M] \]

Since

\[ \frac{d[\text{Cl}]}{dt} = k_1 I_{\text{abs}} - k_2 [\text{Cl}] [\text{Cl}_2] [M] - s[\text{Cl}] = 0 \]

\[ [\text{Cl}] = k_1 I_{\text{abs}}/(k_2 [\text{Cl}_2] [M] + s) \]

and

\[ K \Delta p \propto \frac{k_1 I_{\text{abs}} [M] [\text{Cl}_2]}{(k_2 [\text{Cl}_2] [M] + s)} \]

Since \( M \) may be either of the gases of the mixture \( k_2 [M] \) becomes \( (k_{\text{Cl}_2} [\text{Cl}_2] + k_M [M]) \)

therefore

\[ K \Delta p \propto \frac{k_1 I_{\text{abs}} [\text{Cl}_2] (k_{\text{Cl}_2} [\text{Cl}_2] + k_M [M])}{([\text{Cl}_2] (k_{\text{Cl}_2} [\text{Cl}_2] + k_M [M]) + s)} \]

But \( I_{\text{abs}} \) is constant during the experiment, and if the triple collision coefficients are referred to chlorine as unity, and \( R \) is a constant,

\[ R K \Delta p = \frac{[\text{Cl}_2] ([\text{Cl}_2] + k_M [M])}{[\text{Cl}_2] ([\text{Cl}_2] + k_M [M]) + s} \]

But \( S \) is proportional to the diffusion coefficient of/
of the mixture defined in Mechanism 1.

Hence

\[ R K \Delta p = \left( \frac{[Cl_2]}{([Cl_2] + k_M [M])} \right) \left( \frac{([Cl_2] + k_M [M])}{([Cl_2] + k_M [M]) + m D} \right) \]

Putting \( ([Cl_2] + k_M [M]) = y \)

and \( z = \frac{mD}{[Cl_2]y} \)

we have \( \Delta p = \frac{1}{RK(1 + z)} \)

It should be pointed out that if equation 2 is reversible and the equilibrium

\[ Cl + Cl_2 + M \rightleftharpoons Cl_3 + M \]

is established, the heat then produced in the gas phase can be expressed by an equation of the form

\[ Q \propto [Cl_2] \cdot k_1 \cdot I_{\text{abs}} / (s + k' [Cl_2] [M]) \]

which is of the same general type as before. Present calculations therefore do not admit of distinction being made between these two mechanisms.
4. EXPERIMENTAL PROCEDURE AND RESULTS.

The first step was to calibrate the Bourdon gauge at various pressures. The procedure was as follows:- with the lines between the two sides of the gauge open the vacuum was reduced by admitting dry air through the two-way tap till the manometer $M_1$ registered the approximate pressure at which it was desired to take a reading. The tap to the reaction vessel was then closed and the pressure on the other side of the gauge reduced by the water pump via the low vacuum line, till the gauge pointer registered a reading of between 90 and 100 on the telescope scale, the exact reading being recorded. The vacuum reading of the closed manometer and the pressure reading of the manometer $M_1$ were then taken - the difference being the pressure of gas in the jacket of the Bourdon gauge. Air was then cautiously admitted through the two-way tap till the pointer of the gauge registered between 0 and 5 divisions on the scale. The readings were again taken. From the difference of the readings before and after the admission of air the relation between the pressure variation and the gauge reading was ascertained for that range of pressure. These readings are recorded in Table 7. It is evident from them that the gauge has the same sensitivity throughout the whole/
whole range, and it will be unnecessary therefore later to convert $\Delta p$ from scale divisions to millimetres in the calculations.

The experimental accuracy of any gauge reading may be taken as $\pm 0.1$ divisions of the telescope scale.

**TABLE 7**

Calibration of the Bourdon Gauge

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_0$</td>
<td>$M_1$</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>(mm.)</td>
</tr>
<tr>
<td>738.0</td>
<td>704.0</td>
<td>96.5</td>
<td>2.0</td>
<td>38</td>
<td>4.7</td>
<td>94.5</td>
</tr>
<tr>
<td>740.0</td>
<td>591.5</td>
<td>97.8</td>
<td>4.5</td>
<td>150</td>
<td>4.5</td>
<td>93.3</td>
</tr>
<tr>
<td>742.0</td>
<td>407.0</td>
<td>91.3</td>
<td>2.5</td>
<td>337</td>
<td>4.0</td>
<td>88.8</td>
</tr>
<tr>
<td>745.0</td>
<td>210.0</td>
<td>97.0</td>
<td>3.8</td>
<td>538</td>
<td>4.5</td>
<td>93.2</td>
</tr>
<tr>
<td>747.0</td>
<td>71.0</td>
<td>88.5</td>
<td>1.5</td>
<td>678</td>
<td>4.0</td>
<td>87.0</td>
</tr>
</tbody>
</table>

The mean ratio is 21.03 divisions per mm.

Therefore 1 division of the telescope scale is equal to 0.0476 mm.

Two series of readings were now performed to decide the most suitable pressure of chlorine to use in the main experiments. The two pressures of chlorine used were 45 and 100 mm. Dry air was used as/
as the inert gas. The experimental procedure, which was practically the same as in all subsequent series, was as follows. The reaction vessel having been well chlorinated, and the apparatus thoroughly evacuated, the Hyvac pump was opened direct to the solid chlorine in the tube $T_2$. Any traces of air etc. were removed. The taps were then closed. The flask of liquid air surrounding the chlorine was removed and the solid chlorine allowed to warm gradually. The tap $t_{12}$ was opened. When a small surface layer of liquid chlorine had developed the tap leading to the reaction vessel was slowly opened and chlorine gas allowed to enter. At the same time dry air was admitted to the manometer line through the two-way tap at such a rate as to keep the gauge pointer central. When nearly the required pressure had been admitted to the reaction vessel the tap leading to it and the two-way tap were closed. A little later the tap $t_{12}$ was closed and the liquid air jacket replaced on the chlorine tube. Air was now admitted through the two-way tap till the manometer $M_1$ registered the exact required pressure. Sufficient chlorine had been trapped in the high vacuum line to allow of a further addition to the reaction vessel sufficient to centralize the gauge pointer. When the exact pressure of chlorine had been admitted the tap to the reaction vessel was closed and the tap $t_2$ opened and the residual/
residual chlorine in the high vacuum line was frozen out into the trap \( T_4 \). The high vacuum line was now evacuated with the oil pump to remove any residual traces of chlorine. After the experiments the frozen chlorine in \( T_4 \) was removed by the water pump.

The mercury vapour lamp having been turned on for not less than 30 minutes so that maximum intensity was attained, the copper foil shield was drawn back and the reaction vessel exposed to the light. At the same time the reading of the pointer was noted at the initial equilibrium position, the position of maximum deflection and the final equilibrium position. The shield was then drawn forward and the readings repeated. True experimental equilibrium was only considered to have been attained when the corresponding equilibrium values were substantially constant over a series of readings.

In the initial experiment to decide on the pressure of chlorine to be used, only the true Budde effect (initial equilibrium to maximum deflection) is given, as it was only in this experiment that the "surface adsorption effect" was discovered and its true nature was, of necessity, only realized after the readings were completed. It was however, accurately investigated in the later experiments and the "dry air" experiment was in any case not intended as an accurate series but as a guide to the desirable pressure of chlorine to be used in later work.

The/
The addition of inert gas was performed by a technique sufficiently similar to that of admitting chlorine for description to be unnecessary. After each addition of gas about 15 minutes were allowed for complete mixing. In the special case of the initial series with dry air a slight modification was necessary, the tap between the high vacuum and the manometer lines being opened so that the air which was admitted to the gauge by the two-way tap could also be admitted to the reaction vessel by opening the tap \( t_7 \). The results for the "dry air" series are recorded in Table 8 and plotted in Figure 6.

**TABLE 8.**

<table>
<thead>
<tr>
<th>Pressure of Inert Gas (mm.)</th>
<th>Budde Effect with 45 mm. ( \text{Cl}_2 )</th>
<th>Budde Effect with 100 mm. ( \text{Cl}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.0</td>
<td>4.6</td>
</tr>
<tr>
<td>200</td>
<td>5.2</td>
<td>6.9</td>
</tr>
<tr>
<td>400</td>
<td>7.2</td>
<td>9.0</td>
</tr>
<tr>
<td>600</td>
<td>9.2</td>
<td>10.6</td>
</tr>
</tbody>
</table>
It will be seen from Figure 6 that while the Budde effect with chlorine only is highest with large pressure of chlorine, the slope of the graph is best observed at low pressure. It was decided that 50 mm. chlorine was the most satisfactory compromise between these two factors, as the pressure increase with chlorine only would be sufficient for accurate measurement, while the increase with additions of inert gas was sufficient to allow of accurate study of the inert gas effect.
Measurements of the photoexpansion \((\Delta p)\) for 50 mm. chlorine with varied pressure of the gases nitrogen, oxygen, argon, carbon dioxide and hydrogen chloride were now performed. The results are given in Table 9 and Figure 7.

**TABLE 9**

Variation of the Budde Effect for 50 mm. \(\text{Cl}_2\) with Added Gases.

<table>
<thead>
<tr>
<th>Pressure of Added Gas. (mm.)</th>
<th>(N_2)</th>
<th>(O_2)</th>
<th>(A)</th>
<th>(CO_2)</th>
<th>(HCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>100</td>
<td>3.9</td>
<td>3.7</td>
<td>4.8</td>
<td>4.5</td>
<td>4.4</td>
</tr>
<tr>
<td>200</td>
<td>5.2</td>
<td>5.3</td>
<td>6.3</td>
<td>6.2</td>
<td>7.2</td>
</tr>
<tr>
<td>300</td>
<td>6.4</td>
<td>6.3</td>
<td>8.0</td>
<td>7.7</td>
<td>9.9</td>
</tr>
<tr>
<td>400</td>
<td>7.2</td>
<td>7.1</td>
<td>9.6</td>
<td>9.0</td>
<td>12.1</td>
</tr>
<tr>
<td>500</td>
<td>7.6</td>
<td>8.0</td>
<td>10.7</td>
<td>10.1</td>
<td>15.7</td>
</tr>
<tr>
<td>600</td>
<td>7.9</td>
<td>8.6</td>
<td>11.6</td>
<td>11.2</td>
<td>15.1</td>
</tr>
</tbody>
</table>
The values for HCl prepared from concentrated acid and by photo-synthesis, and for O₂ from cylinders and prepared from calcium carbonate were the same, and accordingly the above figures are the mean of all values obtained. At the same time as these readings were being taken complete study was made of the surface effect and the results have already been given above.

Several methods were tried before a satisfactory one was found for measuring the variation of the /
the Budde effect with alteration of the intensity of light absorbed. A Weston photronic cell was used to measure the intensity of light transmitted, and the variation of sensitivity of this instrument with the wavelength of light is given in Figure 8 (26), on which is also indicated the approximate limits with which light was transmitted by the system, and also absorbed by chlorine.

**Figure 8.**

![Graph showing comparison of sensitivity of photronic cell with wavelengths of light transmitted by system and absorbed by chlorine.](image)

It will be seen from this graph that it was not possible to measure variation of intensity absorbed by difference between the deflections due to the light transmitted, as the light absorbed lies only in a relatively/
relatively insensitive portion of the region of sensitivity, and moreover the sensitivity actually more than doubles between the boundaries of the region of absorption.

With the use of the unimpeded light and through one and two copper gauzes series of readings were obtained over the full range of inert gas pressure related to one another by the constant factors 1 : 1/2 : 1/3 (approximately); but these could not be exactly related to the values derived from the galvanometer readings. With a Chance's ultra-violet plate in the beam of the light the intensity was reduced so much that the Budde effects could no longer be read with any great accuracy, while it was by means certain that the light was thereby rendered effectively monochromatic towards the photronic cell. The rotating sector method was accordingly adopted as the only way of overcoming these difficulties. The sector was inserted between the shutter and the focussing flask. It consisted of a circular frame rotated about its centre, in which alternate quadrants were obscured. A circle round the pivot was also solid, so that the ratio of intensities was not exactly 1 : 0.5. Experiments were first carried out to find the most suitable rate at which to run the sector. When this is very slow the pointer of the gauge/
gauge and the galvanometer spot light swing to and fro, and as the speed increases the limits converge till a steady state is obtained. It was found that when rotated at about 3 revolutions (6 light quadrants) per second there was no noticeable fluctuation, and the actual readings were made at 10-12 revolutions per second. Continuous vision occurs at about 16 revolutions per second, but it was found that if the velocity of rotation was taken as high as this the vibration had an adverse effect on the steadiness of the gauge.

Two series of readings were performed with Argon and HCl as inert gases the ratio of intensities being determined before and after each series.
TABLE 10.

Variation of the Budde effect with altered intensity.

**Argon**

<table>
<thead>
<tr>
<th>Pressure (mm.)</th>
<th>Intensity of Light absorbed</th>
<th>Reduced</th>
<th>Full</th>
<th>Full x 0.535</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2.0</td>
<td>1.0</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.5</td>
<td>1.35</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3.3</td>
<td>1.7</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>4.3</td>
<td>2.2</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

**Hydrogen chloride**

<table>
<thead>
<tr>
<th>Pressure (mm.)</th>
<th>Intensity of Light absorbed</th>
<th>Reduced</th>
<th>Full</th>
<th>Full x 0.535</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.8</td>
<td>0.4</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.7</td>
<td>0.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.3</td>
<td>1.3</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3.3</td>
<td>1.8</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>4.0</td>
<td>2.1</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>4.5</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
</tr>
</tbody>
</table>
It will be seen from Table 10 that the Budde effect is proportional to the intensity of the light absorbed to the attainable accuracy of measurement (± 0.1).

We will now consider which of the three mechanisms outlined above will fit the results given in Tables 9 and 10.

Mechanism 1.

\[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \]

This gave the equation:

\[ R K \Delta p = 2 I_{abs} - \frac{s(\sqrt{s^2 + 8 I_{abs}([\text{Cl}_2] k_{\text{Cl}_2} + [\text{M}] k_{\text{M}}) - s})}{2([\text{Cl}_2] k_{\text{Cl}_2} + [\text{M}] k_{\text{M}})} \]

This formula can be tested at once by reference to the variation of the intensity. For a given gas mixture all the other factors remain constant. If the above mechanism were correct the observed \( \Delta p \) should not be directly proportional to \( I_{abs} \). The results recorded in Table 10 however show that for nitrogen and argon there is strict proportionality over the entire range of pressures.

Further examination of the above equation in relation to \( \Delta p \) for the given conditions (Table 9) shows that even for nitrogen and argon where a constant triple collision efficiency is indicated (27) and
where gas addition offers the minimum disturbance from the point of view of altered wall film, such a formula cannot be made to cover the experimental results. If constants are chosen for the equation to fit one portion of the nitrogen curve of $\Delta p$ plotted against $[N_2]$ the remainder of the curve shows ever increasing divergence, and examination of the corresponding argon series theoretically calculable from the nitrogen curve, leads to similar conclusions. It is therefore deduced that under the given conditions recombination of chlorine atoms does not take place by a process analogous to the recombination processes of bromine and iodine atoms.

**Mechanism 2.**

$$\text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_3$$

$$2 \text{Cl}_3 \rightarrow 3 \text{Cl}_2$$

This gave the kinetic expression

$$R K \Delta p = [\text{Cl}_2] \frac{k_1 I_{abs}}{(S + k_2 [\text{Cl}_2])}.$$  

This equation, it will be noticed, fulfils the requirement of the results in Table 10, since $\Delta p$ is proportional to $I_{abs}$. As, for the results in Table 9, $I_{abs}$ remains constant and independent of added gas, this equation may be put in the form

$$R K \Delta p = \frac{[\text{Cl}_2]}{(S + [\text{Cl}_2])} = \frac{1}{(m D/50 + 1)},$$

where $m$ and $R$ are constants, and $D$ is the factor $(1/D_{\text{Cl}_2} + 1/D_{M})^{-1}$. Apply to this equation the values for/
for $N_2O$ and $N_2$ 300 mm.

$N_2 = 0 \quad K = 0.72 \quad \Delta p = 2.5 \quad D = 5.26 \times 10^{12}$

$R \times 0.72 \times 2.5 = 1/(m \times 5.26 \times 10^{12}/50 + 1) \ldots (1)$

$N_2 = 300 \text{ mm.} \quad K = 2.06 \quad \Delta p = 6.4 \quad D = 1.04 \times 10^{12}$

$R \times 2.06 \times 6.4 = 1/(m \times 1.04 \times 10^{12}/50 + 1) \ldots (2)$

When simplified this becomes

$R \times 19.0 \times 10^{10} \times m + 1.8 R = 1 \ldots \ldots \ldots\ldots (1)$

$R \times 27.45 \times 10^{10} \times m + 13.2 R = 1 \ldots \ldots \ldots\ldots (2)$

Eliminating $m, \quad R = -0.042$

But if $R$ is negative the heat evolved is negative which is impossible. Similarly, eliminating $R, \quad m = -1.345 \times 10^{-10}$

But a negative value of $m$ is impossible, since it would imply that the liberation of heat at the walls brought about an increased liberation of heat in the gas phase, which is the very opposite of the truth. If other results are treated in the same way the same conclusions are reached.

Hence mechanism 2 is untenable as an explanation of the experimental results.

Mechanism 3,

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

$2Cl_3 \rightarrow 3Cl_2$

This gives the formula:

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

where

$z = \frac{mD}{[Cl_2]^2} Y$ and $Y = \left( \left[ Cl_2 \right] + K_M[M] \right)$
The calculations for the various gas mixtures are given in Table 11. Use was made of the following constants:

\[ \sigma_{\text{Cl}_2} = 3.6 \times 10^{-8} \text{ cm.}, \quad \sigma_{\text{N}_2} = 3.1 \times 10^{-8} \text{ cm.}, \quad \sigma_{\text{O}_2} = 2.9 \times 10^{-8} \]

\[ \sigma_{\text{A}} = 2.86 \times 10^{-8} \text{ cm.}, \quad \sigma_{\text{HCl}} = 3.0 \times 10^{-8} \text{ cm.}, \quad \sigma_{\text{CO}_2} = 3.8 \times 10^{-8} \]

\( \sigma_{\text{Cl}} \) was taken as \( 2.0 \times 10^{-8} \text{ cm.} \).

\[ K_{\text{Cl}_2} = 0.72, \quad K_{\text{N}_2} = 2.28, \quad K_{\text{O}_2} = 2.33, \quad K_{\text{A}} = 1.58, \quad K_{\text{CO}_2} = 1.37, \]
and \( K_{\text{HCl}} = 1.61 \) (see Part 3 of this thesis).
### TABLE 11.

Calculation of the Budde Effect results according to Mechanism 3.

\[ \text{Cl}_2 = 50.0 \text{ mm.} \]

<table>
<thead>
<tr>
<th>( m )</th>
<th>( \Delta p ) (calc.)</th>
<th>( \Delta p ) (obs.)</th>
<th>( \Delta p ) calc.</th>
<th>( \Delta p ) obs.</th>
</tr>
</thead>
</table>

#### Nitrogen

\( m = 0.48 \times 10^{-8}, \ k_N = 0.49, \ R = 0.050 \)

<table>
<thead>
<tr>
<th>( m )</th>
<th>( D \times 10^{-13} ) mD/50</th>
<th>( Y )</th>
<th>( Z )</th>
<th>( 1 + Z )</th>
<th>( K )</th>
<th>( \Delta p )</th>
<th>( \Delta p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.26</td>
<td>505</td>
<td>50</td>
<td>10.1</td>
<td>11.1</td>
<td>0.72</td>
<td>2.50</td>
</tr>
<tr>
<td>0.05</td>
<td>2.24</td>
<td>215</td>
<td>99</td>
<td>2.17</td>
<td>3.17</td>
<td>1.65</td>
<td>3.92</td>
</tr>
<tr>
<td>0.10</td>
<td>1.42</td>
<td>131</td>
<td>148</td>
<td>0.68</td>
<td>1.88</td>
<td>1.97</td>
<td>5.40</td>
</tr>
<tr>
<td>0.15</td>
<td>1.04</td>
<td>197</td>
<td>100</td>
<td>0.51</td>
<td>1.51</td>
<td>2.06</td>
<td>6.42</td>
</tr>
<tr>
<td>0.20</td>
<td>0.82</td>
<td>246</td>
<td>79</td>
<td>0.32</td>
<td>1.32</td>
<td>2.10</td>
<td>7.81</td>
</tr>
<tr>
<td>0.25</td>
<td>0.68</td>
<td>295</td>
<td>65</td>
<td>0.23</td>
<td>1.22</td>
<td>2.14</td>
<td>7.66</td>
</tr>
<tr>
<td>0.30</td>
<td>0.58</td>
<td>344</td>
<td>56</td>
<td>0.16</td>
<td>1.16</td>
<td>2.16</td>
<td>7.98</td>
</tr>
</tbody>
</table>

#### Argon

\( m = 0.58 \times 10^{-8}, \ k_A = 0.26, \ R = 0.050 \)

<table>
<thead>
<tr>
<th>( m )</th>
<th>( D \times 10^{-13} ) mD/50</th>
<th>( Y )</th>
<th>( Z )</th>
<th>( 1 + Z )</th>
<th>( K )</th>
<th>( \Delta p )</th>
<th>( \Delta p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.26</td>
<td>610</td>
<td>50</td>
<td>18.2</td>
<td>13.2</td>
<td>0.72</td>
<td>2.51</td>
</tr>
<tr>
<td>0.05</td>
<td>2.33</td>
<td>275</td>
<td>76</td>
<td>3.63</td>
<td>4.63</td>
<td>1.15</td>
<td>4.47</td>
</tr>
<tr>
<td>0.10</td>
<td>1.53</td>
<td>177</td>
<td>103</td>
<td>1.73</td>
<td>2.73</td>
<td>1.41</td>
<td>6.20</td>
</tr>
<tr>
<td>0.15</td>
<td>1.12</td>
<td>130</td>
<td>123</td>
<td>1.015</td>
<td>2.01</td>
<td>1.46</td>
<td>6.07</td>
</tr>
<tr>
<td>0.20</td>
<td>0.90</td>
<td>154</td>
<td>104</td>
<td>0.675</td>
<td>1.67</td>
<td>1.49</td>
<td>9.55</td>
</tr>
<tr>
<td>0.25</td>
<td>0.74</td>
<td>180</td>
<td>85</td>
<td>0.48</td>
<td>1.48</td>
<td>1.50</td>
<td>10.7</td>
</tr>
<tr>
<td>0.30</td>
<td>0.63</td>
<td>206</td>
<td>73</td>
<td>0.35</td>
<td>1.35</td>
<td>1.52</td>
<td>11.6</td>
</tr>
</tbody>
</table>

#### Oxygen

\( m = 0.54 \times 10^{-8}, \ k_{O_2} = 0.54, \ R = 0.045 \)

<table>
<thead>
<tr>
<th>( m )</th>
<th>( D \times 10^{-13} ) mD/50</th>
<th>( Y )</th>
<th>( Z )</th>
<th>( 1 + Z )</th>
<th>( K )</th>
<th>( \Delta p )</th>
<th>( \Delta p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.26</td>
<td>683</td>
<td>50</td>
<td>11.35</td>
<td>12.35</td>
<td>0.72</td>
<td>2.50</td>
</tr>
<tr>
<td>0.05</td>
<td>2.29</td>
<td>247</td>
<td>104</td>
<td>2.57</td>
<td>3.57</td>
<td>1.79</td>
<td>3.68</td>
</tr>
<tr>
<td>0.10</td>
<td>1.33</td>
<td>143</td>
<td>158</td>
<td>0.905</td>
<td>1.905</td>
<td>2.01</td>
<td>4.80</td>
</tr>
<tr>
<td>0.15</td>
<td>1.08</td>
<td>212</td>
<td>117</td>
<td>0.55</td>
<td>1.55</td>
<td>2.10</td>
<td>6.62</td>
</tr>
<tr>
<td>0.20</td>
<td>0.85</td>
<td>266</td>
<td>92</td>
<td>0.35</td>
<td>1.35</td>
<td>2.15</td>
<td>7.64</td>
</tr>
<tr>
<td>0.25</td>
<td>0.70</td>
<td>320</td>
<td>75.6320</td>
<td>0.24</td>
<td>1.24</td>
<td>2.18</td>
<td>8.20</td>
</tr>
<tr>
<td>0.30</td>
<td>0.59</td>
<td>374</td>
<td>63.7374</td>
<td>0.17</td>
<td>1.17</td>
<td>2.21</td>
<td>8.60</td>
</tr>
</tbody>
</table>
### Table 11 (contd.)

<table>
<thead>
<tr>
<th>Hydrogen chloride</th>
<th>m = 0.83 x 10^{-8}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_{HCl} = 0.26, R = 0.0605</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>D x 10^{-12} mm (D)</th>
<th>Y</th>
<th>Z</th>
<th>l + z</th>
<th>K</th>
<th>Δp (calc.)</th>
<th>Δp (obs.)</th>
<th>Δp calc.</th>
<th>Δp obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.26</td>
<td>873</td>
<td>50</td>
<td>17.4</td>
<td>18.4</td>
<td>0.72</td>
<td>2.50</td>
<td>2.5</td>
</tr>
<tr>
<td>100</td>
<td>2.19</td>
<td>364</td>
<td>76</td>
<td>4.79</td>
<td>5.79</td>
<td>1.30</td>
<td>4.40</td>
<td>4.4</td>
</tr>
<tr>
<td>200</td>
<td>1.38</td>
<td>229</td>
<td>102</td>
<td>2.24</td>
<td>3.24</td>
<td>1.42</td>
<td>7.19</td>
<td>7.2</td>
</tr>
<tr>
<td>300</td>
<td>1.01</td>
<td>168</td>
<td>128</td>
<td>1.31</td>
<td>2.31</td>
<td>1.47</td>
<td>9.75</td>
<td>9.9</td>
</tr>
<tr>
<td>400</td>
<td>0.74</td>
<td>123</td>
<td>154</td>
<td>0.80</td>
<td>1.80</td>
<td>1.50</td>
<td>12.2</td>
<td>12.1</td>
</tr>
<tr>
<td>500</td>
<td>0.66</td>
<td>109</td>
<td>190</td>
<td>0.61</td>
<td>1.61</td>
<td>1.52</td>
<td>13.5</td>
<td>13.7</td>
</tr>
<tr>
<td>600</td>
<td>0.555</td>
<td>92</td>
<td>206</td>
<td>0.45</td>
<td>1.45</td>
<td>1.53</td>
<td>14.9</td>
<td>15.1</td>
</tr>
</tbody>
</table>

### Carbon dioxide

| m = 0.455 x 10^{-8}, |
| k_{CO_2} = 0.13, R = 0.0518 |

<table>
<thead>
<tr>
<th>D x 10^{-12} mm (D)</th>
<th>Y</th>
<th>Z</th>
<th>l + z</th>
<th>K</th>
<th>Δp (calc.)</th>
<th>Δp (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.26</td>
<td>479</td>
<td>50</td>
<td>9.58</td>
<td>10.58</td>
<td>0.72</td>
</tr>
<tr>
<td>100</td>
<td>2.02</td>
<td>194</td>
<td>63</td>
<td>2.92</td>
<td>3.92</td>
<td>1.15</td>
</tr>
<tr>
<td>200</td>
<td>1.25</td>
<td>114</td>
<td>76</td>
<td>1.50</td>
<td>2.50</td>
<td>1.24</td>
</tr>
<tr>
<td>300</td>
<td>0.90</td>
<td>82.4</td>
<td>89</td>
<td>0.925</td>
<td>1.93</td>
<td>1.28</td>
</tr>
<tr>
<td>400</td>
<td>0.76</td>
<td>69.5</td>
<td>102</td>
<td>0.69</td>
<td>1.69</td>
<td>1.30</td>
</tr>
<tr>
<td>500</td>
<td>0.53</td>
<td>53.1</td>
<td>115</td>
<td>0.46</td>
<td>1.46</td>
<td>1.31</td>
</tr>
<tr>
<td>600</td>
<td>0.495</td>
<td>45.0</td>
<td>128</td>
<td>0.35</td>
<td>0.35</td>
<td>1.32</td>
</tr>
</tbody>
</table>
It will be observed that the above expression gives calculated values in good agreement with the experimental results. In Figure 7 the curves for the various gases are drawn from the theoretical values according to Mechanism 3, while the points marked are the observed pressure differences. It does not appear that any better curves could be drawn through these points. The values of the constants m and R are sensibly the same for N₂, Ar, O₂ and CO₂, although for HCl, m is somewhat greater and R less. The constant m expresses the rate at which atoms reach the wall and are removed; the high value for HCl would therefore indicate a greater efficiency of adsorption of chlorine atoms by a surface carrying adsorbed HCl, in agreement with previous conclusions.

In considering the values of k as used in the above table, it is to be remembered that such values represent relative triple collision velocity coefficients only when stabilization of Cl₅ is concerned; if any other reaction occurs, k would give relative values for the product of heat of reaction and velocity coefficient. For Cl₂, N₂ and Ar where the Cl₅ stabilization is the only probable process, the k values, taking k₅ as unity, are 2.03, 1.00 and 0.53 respectively.

In/
In table 12 the relative values of the triple collision coefficients, \( k_{N_2} \) taken as unity, are compared with values obtained by workers on other reactions.

**TABLE 12.**

Comparison of values for triple collision coefficients.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HCl</th>
<th>Cl(_2)</th>
<th>CO(_2)</th>
<th>O(_2)</th>
<th>N(_2)</th>
<th>A</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br + Br</td>
<td></td>
<td></td>
<td>1.13</td>
<td>1.12</td>
<td>1.0</td>
<td>0.63</td>
<td>(5)</td>
</tr>
<tr>
<td>Br + Br</td>
<td></td>
<td></td>
<td>2.16</td>
<td>1.28</td>
<td>1.0</td>
<td>0.52</td>
<td>(28)</td>
</tr>
<tr>
<td>Br + Br</td>
<td></td>
<td></td>
<td>1.38</td>
<td>1.38</td>
<td>1.0</td>
<td>0.64</td>
<td>(29)</td>
</tr>
<tr>
<td>I + I</td>
<td></td>
<td></td>
<td>2.72</td>
<td>1.59</td>
<td>1.0</td>
<td>0.58</td>
<td>(30)</td>
</tr>
<tr>
<td>Cl + Cl(_2)</td>
<td>0.53</td>
<td>2.03</td>
<td>0.27</td>
<td>1.10</td>
<td>1.0</td>
<td>0.53</td>
<td>Present values</td>
</tr>
<tr>
<td>Cl + NCl(_3)</td>
<td>2.24</td>
<td>2.24</td>
<td>1.47</td>
<td>1.0</td>
<td>0.94</td>
<td></td>
<td>(31)</td>
</tr>
<tr>
<td>H + O(_2)</td>
<td>5.4</td>
<td>3.57</td>
<td>2.23</td>
<td>0.58</td>
<td>1.0</td>
<td>0.60</td>
<td>(37)</td>
</tr>
<tr>
<td>O + O(_2)</td>
<td></td>
<td></td>
<td>0.44</td>
<td>1.0</td>
<td>0.63</td>
<td></td>
<td>(32)</td>
</tr>
<tr>
<td>O + O(_2)</td>
<td></td>
<td></td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.2</td>
<td>(33)</td>
</tr>
</tbody>
</table>

The \( k_{N_2} : k_A \) ratio compares very favourably with ratios determined in other stabilizations \((O_3, Br_2, I_2, HO_2)\); the value for oxygen \((1.10)\) is similarly in agreement with the conclusions of Rabinovitch and Wood \((17)\), that such efficiency is higher for diatomic than for monatomic molecules, and increases with growing molecular size and the intensity of the molecular fields of the colliding particles.
particles. The value for $k_{\text{HCl}} / k_{\text{N}_2} (0.53)$ here obtained is considerably different from that recorded in the H-O$_2$ reaction (Ritchie, (27)) where the value is 5.4; the present value may be more consistent with size and molecular weight than the higher figure, obtained for a triple collision which may not result in the stabilization of HO$_2$, but which may give as products H$_2$O and ClO.

The ratio $k_{\text{CO}_2} : k_{\text{N}_2} = 0.27$ is much less than the ratios obtained in other stabilizations (1.4 to 2.7), and it is difficult to visualize other suitable reactions which might occur on the collision of Cl, Cl$_2$ and CO$_2$. In the examination of the Budde effect in bromine (5), carbon dioxide was abnormal in that no constant values of m and R could be found to fit experimental results over the entire pressure range, a progressive change in surface conditions being regarded as responsible; it is possible that the small value of 0.27 may not be unconnected with similar phenomena. It may also be of importance in this connection that the "adsorption effect" discussed earlier was not observed for Cl$_2$ - CO$_2$ and Cl$_2$ - HCl mixtures, and this may be taken to indicate a difference in surface conditions in these gases when compared with the more permanent gases N$_2$, Ar, and O$_2$. It is possible that conditions in the presence of CO$_2$ and HCl are not to be regarded as comparable with those in the presence of/
of the other gases, and accordingly while the values of the triple collision coefficients of these gases may be compared with each other, they cannot be compared with those for \( N_2 \), \( O_2 \), and \( Ar \). It will be seen that the value for \( k_{\text{HCl}} \) is twice that for \( k_{\text{CO}_2} \), which is in conformity with the results of other workers.

The effect of water vapour on the Budde effect was now studied. As the light system had been upset by the introduction of the rotating sector for the intensity measurements, a new standard series with nitrogen as the inert gas was carried out, while for \( \text{HCl} \) and \( \text{CO}_2 \) the proportional values are calculated from the new nitrogen figures. Three series were now carried out with nitrogen as the inert gas, two with 11 mm. of water vapour and the third with 2 mm. of water vapour. The values were substantially the same. In the same way series were performed with \( \text{HCl} \) and \( \text{CO}_2 \) as inert gases with 2 mm. of water vapour. A long evacuation without baking-out was performed, and a series with dry nitrogen now gave results almost the same as those with 2 mm. of water.

The reaction vessel was now baked-out by building an asbestos oven round it which was heated by Meker burners to 300°C. At the same time the vessel was evacuated by the mercury vapour pump backed by the Hyvac pump. After two days' treatment the oven was dismantled/
dismantled and the light system replaced. The intensity was adjusted to the same value by the help of the photronic cell system. A series with nitrogen as the inert gas was then carried out. The oven was refitted and the procedure repeated, except that the treatment was carried out for three hours only. A repetition of the nitrogen series gave concordant results. A series with nitrogen and 2 mm. of water vapour was now twice performed with results substantially concordant with those before baking-out.

**TABLE 13**

**Effect of water vapour on magnitude of Budde effect.**

<table>
<thead>
<tr>
<th>State of Vessel</th>
<th>Inert Gas Pressure (mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td><strong>N₂</strong></td>
<td></td>
</tr>
<tr>
<td>Baked out</td>
<td>3.1</td>
</tr>
<tr>
<td>2 mm. water</td>
<td>2.9</td>
</tr>
<tr>
<td>Long evacuation</td>
<td>2.8</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td></td>
</tr>
<tr>
<td>2 mm. water</td>
<td>2.9</td>
</tr>
<tr>
<td>Normal (calculated)</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>HCl</strong></td>
<td></td>
</tr>
<tr>
<td>2 mm. water</td>
<td>2.9</td>
</tr>
<tr>
<td>Normal (calculated)</td>
<td>2.7</td>
</tr>
</tbody>
</table>
It will be seen from the above results that the differences resultant on baking out and on the addition of water vapour are small. The baked out value is slightly higher at low pressures, but this difference disappears at high pressure of inert gas. This is in agreement with Craggs and Allmand (loc. cit.) who found that the addition of water vapour slightly decreased the rate of photo-synthesis of hydrogen chloride under conditions where surface action was appreciable; a surface carrying adsorbed water was considered slightly more efficient in removing chain carriers.

Where HCl and CO₂ are the inert gases there is good concordance between the normal and wet readings, suggesting that in the presence of these gases water has no appreciable modifying action on the wall. Rodebush and Spealman (34) in studying the reaction of hydrogen atoms with HCl found that the presence or absence of water vapour has no effect on the adsorbed layer of HCl in conformity with the above conclusions. It is of interest in this connection to quote the results of Whytlaw-Gray and his co-workers (35 and 36) and of Moles (37 and 38) on the adsorption of gases on glass and silica. As a silica vessel was used in Part 3 of this work, we may conveniently consider here their results with both types of surfaces.

Silica/
Silica and glass behave quite differently as regards adsorbed gas. With silica not only is the amount of gas given off much smaller, but it comes off completely on one evacuation, whilst from glass it comes off slowly and is only finally eradicated after prolonged treatment. The gas removable from a silica surface is perfectly constant, while from glass it depends on the previous history and treatment of the vessel. Hartley, Henry and Whytlaw-Gray (35) give the following figures for volumes of gas adsorbed in c.c. x 10⁻⁶ per sq. cm. of surface at different pressures at 21°C. on silica.

**TABLE 14**

Adsorption of gases on silica at 21°C.
(c.c. per sq. cm. x 10⁶).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure in mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>760</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.45</td>
</tr>
<tr>
<td>N₂</td>
<td>0.74</td>
</tr>
<tr>
<td>Ar</td>
<td>0.42</td>
</tr>
<tr>
<td>O₂</td>
<td>0.20</td>
</tr>
</tbody>
</table>

They give the following table of comparison between their results for silica and those of Moles for glass (37). The third column in the table is inserted to give another set of results by Moles (38) stated to be made under the same conditions.
TABLE 15.

Adsorption on glass at 760 mm. and room temperature. (c.c. per sq. cm. x 10^6)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Silica</th>
<th>Soda Glass</th>
<th>Soda Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.44</td>
<td>89</td>
<td>89.5</td>
</tr>
<tr>
<td>N₂</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar</td>
<td>0.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>0.20</td>
<td>41</td>
<td>39.0</td>
</tr>
<tr>
<td>HCl</td>
<td>-</td>
<td>-</td>
<td>210.0</td>
</tr>
</tbody>
</table>

Burt and Whytlaw-Gray (36) stated that HCl was adsorbed on glass almost directly proportionally to its pressure, and that the correction to pressure amounted to 1 part in 10,300. These figures lead us to the conclusion that HCl and CO₂ are very much more readily adsorbed than the other three gases we have used, and it is not improbable that in their presence the wall consists effectively of molecules of these gases regardless of the presence or absence of water vapour, whereas for N₂, O₂ and Ar, water vapour will without doubt modify the nature of the surface very considerably. A factor also tending in the same direction may be the comparatively great solubility of the former two gases in water.
5. **SUMMARY AND CONCLUSIONS.**

The results obtained for the Budde effect in chlorine are consistent with the mechanism:

1. \( \text{Cl}_2 + h\gamma \rightarrow \text{Cl} + \text{Cl} \)
2. \( \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_3 + M \)
3. \( 2 \text{Cl}_3 \rightarrow 3\text{Cl}_2 \)
4. \( \text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2 \) (at wall)

which gives the kinetic expression:

\[
\mathbf{R} \mathbf{K} \Delta \mathbf{P} = \frac{\text{Cl}_2 \left[ \text{Cl}_2 + k_\text{M} M \right]}{\left( \text{Cl}_2 \left[ \text{Cl}_2 + k_\text{M} M \right] + mD \right)}
\]

They are not consistent with any other mechanism which has been suggested.

A new effect has been observed during the making of these observations, which can be explained in strict conformity with the mechanism, and, in fact, may be held to form an additional proof thereof. This is, that with certain gas mixtures the gauge pointer, both on exposing the light and masking it, after attaining the deflection which constitutes the true Budde effect, moves back to a position slightly less than the point of maximum deflection. This is explained on the assumption that a species (namely the \( \text{Cl}_3 \) molecule) is formed as a result of the reaction which is adsorbed on the surface of the wall, and is sufficiently stable thereon for an appreciable concentration to be built up, but is slowly desorbed again/
again, though whether as such, or as a result of reaction to form the normal Cl₂ molecules, it has not been found possible to establish. In accordance with this explanation, the effect is at a minimum at zero and at high pressures of inert gas, i.e. when there are too few third bodies to permit of reaction 2 proceeding at such a rate as to build up an appreciable concentration, and when the pressure of inert gas is so great that the Cl₃ molecules, though formed in increased numbers, are unable to diffuse to the wall before being decomposed by reaction 3. The effect reaches a maximum at an intermediate pressure, namely 300 mm., where the concentration on the walls was equivalent to 0.038 mm.

It has not been found possible to establish whether or not reaction 2 is reversible, as the kinetic expression is of the same form in both cases.

The absence of the "surface effect" referred to above when CO₂ and HCl are the inert gases, has been explained as due to a changed condition of the wall due to their presence. The high values for the constant m for HCl in the kinetic expression indicates a greater efficiency of adsorption of Cl atoms by a surface carrying adsorbed HCl. The low value for the triple collision coefficient for CO₂ can scarcely be explained as due to some other reaction resulting on the collision Cl - Cl₂ - CO₂. Both these factors are therefore held to/
to be an additional suggestion of abnormality of the surface in the presence of these gases as compared to the condition when the "permanent" gases are used as third bodies.

The effect of water vapour on the Budde effect is slight. The baked out value is slightly higher at low pressure, but this difference disappears at high pressure of inert gas. These results confirm the view of Craggs and Allmand that a wet wall is slightly more efficient in adsorbing chlorine atoms or Cl₃ complexes. Where HCl or CO₂ are present the results are almost identical regardless of the presence or absence of water vapour, and the results of Whytlaw-Grey and his co-workers are quoted to show that these gases are adsorbed on a glass surface to a much greater extent than the so-called "permanent" gases. The abnormal nature of HCl and CO₂ is regarded as consistent throughout all the experiments.

It appears probable from the Budde effect results, that in any reaction involving chlorine, where the recombination of chlorine atoms is of importance, added inert gas or products of reaction will tend to reduce the concentration of chlorine atoms by means of the triple collision process:

\[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \]

The rate of photo-combination of hydrogen and chlorine should be retarded, under certain conditions, by the product hydrogen chloride.
PART 2.

THE THERMAL CONDUCTIVITY
OF CERTAIN GASES AND GAS MIXTURES.
1. INTRODUCTION.

As already stated in the General Introduction, no value could be found in published work for the thermal conductivity of hydrogen-chloride; and the assumption, that the thermal conductivity of the mixtures of chlorine with other gases used in the measurement of the photo-expansion, could be taken as the sum of partial values, required some experimental justification. Considerable divergence from this rule takes place with some gas mixtures, more particularly those approaching a 50/50% composition, according to the scanty data available in published papers.

The method employed was the standard one, originated by Schleiermacher (39), of measuring the change of resistance of a hot wire in the various gases and gas mixtures. The electrical circuit employed was the "constant voltage" type (40). The general conductivity equation is \( \Delta Q = K A \Delta T / d \), where \( \Delta Q \) is the quantity of heat transferred per second across an area \( A \), \( \Delta T \) is the difference in temperature between two planes at a distance \( d \), and \( K \) is the thermal conductivity of the medium between the two planes. The potential across the Wheatstone bridge was kept constant, and hence as the resistance of/
of the filament wire rose, the potential across it increased, while the current dropped. The product, which is the electrical energy expended in the wire, remained very constant. Hence since $\Delta Q$ is approximately constant $K \propto 1/\Delta T$. But the resistance of the filament must obey the general expression for the change of resistance of a wire with increase in its temperature; $R_f = R_0 (1 + \alpha T)$. But $R_0$, the resistance of the wire at a standard temperature, and $\alpha$, the temperature coefficient of resistance of the metal, are constants for the system.

$$\frac{d R_f}{d T} = R_0 \alpha,$$

or

$$\Delta R_f \propto \Delta T.$$

But $K \propto 1/\Delta T$, and therefore $K \propto 1/\Delta R_f$. But if the variable resistance $R$ of the Wheatstone bridge is the opposite arm of this circuit to the filament, $R$ is inversely proportional to $R_f$. Therefore $K/\Delta R = \text{constant}$. From this we may deduce that the relationship between conductivity and value of the resistance $R$ for any three gases, whose conductivities are $K$, $K_1$ and $K_2$, and which give values for the variable resistance of $R$, $R_1$ and $R_2$, will be given by

$$\frac{(K - K_1)}{(R - R_1)} = \frac{(K_1 - K_2)}{(R_1 - R_2)},$$

or in the form found most suitable for numerical substitution

$$K = K_1 + (K_2 - K_1)\frac{(R_1 - R)}{(R_1 - R_2)}.$$
It was unnecessary for the present purpose to measure absolute values, and accordingly relative conductivity measurements only were made, and converted to absolute values by reference to the corresponding quantities for the known gases. For comparative values the resistance of the leads to the conductivity vessel may be neglected, as these constitute a constant correction which is cancelled out in comparison.

It is customarily assumed that the thermal conductivity of a gas is independent of its pressure. This is not strictly the case, although Maxwell, from a consideration of the kinetic theory of gases, predicted that there should be no change over a wide variation. This depends on the fact that halving the number of molecules by halving the pressure allows the molecules to travel twice as far. However, if the pressure is lowered so that the mean free path of the molecule becomes comparable with the size of the vessel the thermal conductivity increases. The results of Senftleben and Reichmar (41) show that for their apparatus the conductivity of gases such as here considered reached a steady value at about 10 mm. The vessel here used is much larger and therefore the limit will be smaller. We shall accordingly assume that the conductivity of all the gases used are constant in the region 50 - 650 mm. here studied.
2. DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE.

The apparatus employed was basically the same as that described in Part 1 of this thesis, with the following modifications. The reaction vessel was cut off and joined to the female portion of a ground glass joint. The male portion was rounded off at its free end and two thin glass tubes were sealed through this end. One tube was 7 cm. shorter than the other, and they were of such length that when the reaction vessel was fitted on by the ground glass joint the midpoint between the two ends was in the centre of the flask. Short pieces of 0.5 mm. diameter platinum wire were sealed through the ends of the tubes. A straight Pt filament 7 cm. long and 0.0076 cm. diameter was spot welded to the two thick Pt wires. The other ends of the Pt wires were connected to the leads from the electrical circuit by mercury contacts in the thin tubes. A T-piece was made in the tube between the male joint and the end seal to connect the conductivity vessel to the gauge and the tap t. Figure 9 shows the details of this portion of the apparatus.
The electrical circuit is given in Figure 10. It consists of a source of direct current derived from large accumulators, and reduced to a suitable voltage by a potentiometer; and a normal Wheatstone bridge circuit. The conductivity flask was thermostated in a water bath in the usual manner. All gases were prepared and purified as in Part 1, except that HCl was only prepared from the concentrated acid.

The conductivity vessel was thoroughly evacuated, and the potential across the bridge adjusted to a constant value of about 4 volts. This made the potential across the filament about 2 volts, which gave a heat evolution, as measured by the increase of pressure, comparable with, but slightly greater than, that in the Buide effect measurements, and made the wire glow a very dull red. The Wheatstone bridge was now balanced. 10 ohms and 5000 ohms were found convenient values for the two fixed arms, and these were used throughout. The value for the variable resistance at balance for complete vacuum was then read. While this value can theoretically be made use of in calculations of conductivities, it is so susceptible to the least traces of any gas that it was found more convenient to use it only as a very accurate check on the complete evacuation of the vessel. All the unknown values to be determined lie within the range covered by the known values for single gases.
50 mm. of a particular gas were now admitted by the usual technique, and the bridge accurately balanced. The value of the variable resistance was noted. Another 100 mm. of the same gas were now admitted and the same procedure gone through. This was repeated up to 650 mm. pressure of each gas. Measurements were made in this way with \( O_2 \), \( N_2 \), HCl, and \( CO_2 \).

50 mm. of chlorine alone were admitted to the evacuated conductivity vessel, the bridge balanced and the variable resistance measurement recorded. Then oxygen was admitted 100 mm. at a time with corresponding measurements until a mixture of 50 mm. \( Cl_2 \) and 600 mm. \( O_2 \) was reached. This procedure was repeated with the other gases.
3. RESULTS AND CALCULATIONS.

The following results were obtained for the value of the variable resistance with the single gases studied.

TABLE 16.

<table>
<thead>
<tr>
<th>Pressure of Gas (mm.)</th>
<th>Value of Variable Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( N_2 )</td>
</tr>
<tr>
<td>50</td>
<td>2246</td>
</tr>
<tr>
<td>150</td>
<td>2197</td>
</tr>
<tr>
<td>250</td>
<td>2171</td>
</tr>
<tr>
<td>350</td>
<td>2147</td>
</tr>
<tr>
<td>450</td>
<td>2132</td>
</tr>
<tr>
<td>550</td>
<td>2119</td>
</tr>
<tr>
<td>650</td>
<td>2106</td>
</tr>
</tbody>
</table>

Contrary to expectation the resistance of the wire did not remain at constant value for different pressures of added gas, but decreased regularly as the pressure was increased. Taking the resistance at single gas pressure of 50 mm. as standard however, it is found that the same corrections for all gases restores the compensating resistance (inversely proportional to the resistance of the filament) to the standard values for 50 mm.

The values of the corrections are given in Table 17.
### TABLE 17.

<table>
<thead>
<tr>
<th>Pressure of Gas (mm.)</th>
<th>Correction (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>150</td>
<td>49</td>
</tr>
<tr>
<td>250</td>
<td>75</td>
</tr>
<tr>
<td>350</td>
<td>99</td>
</tr>
<tr>
<td>450</td>
<td>114</td>
</tr>
<tr>
<td>550</td>
<td>127</td>
</tr>
<tr>
<td>650</td>
<td>140</td>
</tr>
</tbody>
</table>

Convection currents are considered to be the cause of the divergence from the expected constant values. The heat evolution is here concentrated at the surface of a short wire in a large vessel, a condition likely to give rise to very much greater convection than the more even distribution of heat evolution throughout the gas phase occurring in the Budde effect experiments. It is accordingly considered justifiable to correct here for the convection effect, and assume that any such effect is negligible in the photo-expansion results. Since the same correction is applicable to all single gases studied, it is considered applicable to mixtures of chlorine with these gases. If we apply the mean corrections to values obtained for R with the various pressures of HCl, we get an average value for R<sub>50 mm. </sub> Cl<sub>2</sub> of 2439.4 ohms.
If \( x \) and \( y \) are any two standard gases, then the thermal conductivity of any other gas is given by

\[
K = K_x + (R_x - R)(K_y - K_x)/(R_x - R_y)
\]

where \( R \) is the value of the compensating resistance.

In the case of chlorine and nitrogen this becomes

\[
K = K_{\text{Cl}_2} + (R_{50 \ \text{Cl}_2} - R)(K_{\text{N}_2} - K_{\text{Cl}_2})/(R_{50 \ \text{Cl}_2} - R_{50 \ \text{N}_2})
\]

\[
= 0.718 + (2700 - R)(2.28 - 0.818)/(2700 - 2246)
\]

\[
= 0.718 + (2700 - R) \times 0.003435
\]

An expression giving practically identical values for \( K \) may also be obtained from other suitable pairs of gases e.g. \( \text{Cl}_2/\text{O}_2 \), \( \text{Cl}_2/\text{CO}_2 \), \( \text{N}_2/\text{CO}_2 \), or \( \text{O}_2/\text{CO}_2 \).

By the use of the equation we get

\[
K_{\text{HCl}} = 0.718 + (2700 - 2439.4) \times 0.003435
\]

\[
= 1.61.
\]

The following values for the variable resistance were obtained with mixtures of 50 mm. \( \text{Cl}_2 \) with varied pressure of other gases.

**TABLE 18**

<table>
<thead>
<tr>
<th>Added Gas (mm.)</th>
<th>( \text{N}_2 )</th>
<th>( \text{O}_2 )</th>
<th>( \text{HCl} )</th>
<th>( \text{CO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2700</td>
<td>2700</td>
<td>2700</td>
<td>2700</td>
</tr>
<tr>
<td>100</td>
<td>2344</td>
<td>2339</td>
<td>2452</td>
<td>2528</td>
</tr>
<tr>
<td>200</td>
<td>2250</td>
<td>2237</td>
<td>2383</td>
<td>2471</td>
</tr>
<tr>
<td>300</td>
<td>2202</td>
<td>2189</td>
<td>2337</td>
<td>2436</td>
</tr>
<tr>
<td>400</td>
<td>2174</td>
<td>2160</td>
<td>2318</td>
<td>2412</td>
</tr>
<tr>
<td>500</td>
<td>2148</td>
<td>2158</td>
<td>2393</td>
<td>2395</td>
</tr>
<tr>
<td>600</td>
<td>2132</td>
<td>2115</td>
<td>2278</td>
<td>2379</td>
</tr>
</tbody>
</table>
In Table 19 the above values are corrected in accordance with Table 17, and from the corrected values so obtained the corresponding values for the thermal conductivity of the gas mixtures are calculated by the above equation. In the same table are recorded the values for the conductivity of gas mixtures obtained by the formula assuming conductivity to be a linear function of composition

\[ K = (K_M - K_{\text{Cl}_2}) \frac{[M]}{([\text{Cl}_2] + [M])} + K_{\text{Cl}_2} \]

where the values for single gases are

- \( \text{Cl}_2 \) 0.718
- \( \text{N}_2 \) 2.28
- \( \text{O}_2 \) 2.33
- \( \text{HCl} \) 1.61
- \( \text{CO}_2 \) 1.37

Also from the theoretical values so derived a reverse calculation is made of the variable resistance. A comparison between the values of the resistance so obtained shows good agreement between the two. The smallest change in the variable resistance \( R \) to which the galvanometer was definitely sensitive was 1 ohm.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mm. chlorine with varied nitrogen.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2700</td>
<td>-</td>
<td>2700</td>
<td>0.718</td>
<td>0.718</td>
<td>2700</td>
<td>2700</td>
</tr>
<tr>
<td>100</td>
<td>2344</td>
<td>48</td>
<td>2392</td>
<td>1.75</td>
<td>1.76</td>
<td>2396</td>
<td>2348</td>
</tr>
<tr>
<td>200</td>
<td>2250</td>
<td>76</td>
<td>2326</td>
<td>1.97</td>
<td>1.97</td>
<td>2328</td>
<td>2250</td>
</tr>
<tr>
<td>300</td>
<td>2220</td>
<td>98</td>
<td>2300</td>
<td>2.06</td>
<td>2.06</td>
<td>2300</td>
<td>2202</td>
</tr>
<tr>
<td>400</td>
<td>2174</td>
<td>114</td>
<td>2288</td>
<td>2.10</td>
<td>2.10</td>
<td>2288</td>
<td>2174</td>
</tr>
<tr>
<td>500</td>
<td>2148</td>
<td>128</td>
<td>2276</td>
<td>2.14</td>
<td>2.14</td>
<td>2276</td>
<td>2148</td>
</tr>
<tr>
<td>600</td>
<td>2132</td>
<td>140</td>
<td>2272</td>
<td>2.15</td>
<td>2.16</td>
<td>2270</td>
<td>2130</td>
</tr>
<tr>
<td>50 mm. chlorine with varied oxygen.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2700</td>
<td>-</td>
<td>2700</td>
<td>0.718</td>
<td>0.718</td>
<td>2700</td>
<td>2700</td>
</tr>
<tr>
<td>100</td>
<td>2339</td>
<td>48</td>
<td>2387</td>
<td>1.76</td>
<td>1.79</td>
<td>2388</td>
<td>2340</td>
</tr>
<tr>
<td>200</td>
<td>2337</td>
<td>76</td>
<td>2313</td>
<td>2.01</td>
<td>2.01</td>
<td>2315</td>
<td>2339</td>
</tr>
<tr>
<td>300</td>
<td>2189</td>
<td>98</td>
<td>2287</td>
<td>2.10</td>
<td>2.10</td>
<td>2287</td>
<td>2189</td>
</tr>
<tr>
<td>400</td>
<td>2160</td>
<td>114</td>
<td>2274</td>
<td>2.14</td>
<td>2.15</td>
<td>2275</td>
<td>2159</td>
</tr>
<tr>
<td>500</td>
<td>2158</td>
<td>128</td>
<td>2266</td>
<td>2.17</td>
<td>2.18</td>
<td>2264</td>
<td>2156</td>
</tr>
<tr>
<td>600</td>
<td>2115</td>
<td>140</td>
<td>2255</td>
<td>2.21</td>
<td>2.21</td>
<td>2255</td>
<td>2115</td>
</tr>
<tr>
<td>50 mm. chlorine with varied hydrogen-chloride.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2700</td>
<td>-</td>
<td>2700</td>
<td>0.718</td>
<td>0.718</td>
<td>2700</td>
<td>2700</td>
</tr>
<tr>
<td>100</td>
<td>2452</td>
<td>48</td>
<td>2500</td>
<td>1.30</td>
<td>1.31</td>
<td>2497</td>
<td>2449</td>
</tr>
<tr>
<td>200</td>
<td>2333</td>
<td>76</td>
<td>2459</td>
<td>1.48</td>
<td>1.43</td>
<td>2456</td>
<td>2380</td>
</tr>
<tr>
<td>300</td>
<td>2337</td>
<td>98</td>
<td>2435</td>
<td>1.49</td>
<td>1.48</td>
<td>2438</td>
<td>2340</td>
</tr>
<tr>
<td>400</td>
<td>2318</td>
<td>114</td>
<td>2432</td>
<td>1.50</td>
<td>1.51</td>
<td>2428</td>
<td>2314</td>
</tr>
<tr>
<td>500</td>
<td>2339</td>
<td>128</td>
<td>2436</td>
<td>1.53</td>
<td>1.53</td>
<td>2431</td>
<td>2393</td>
</tr>
<tr>
<td>600</td>
<td>2378</td>
<td>140</td>
<td>2418</td>
<td>1.54</td>
<td>1.54</td>
<td>2418</td>
<td>2378</td>
</tr>
<tr>
<td>50 mm. chlorine with varied carbon dioxide.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2700</td>
<td>-</td>
<td>2700</td>
<td>0.718</td>
<td>0.718</td>
<td>2700</td>
<td>2700</td>
</tr>
<tr>
<td>100</td>
<td>2526</td>
<td>48</td>
<td>2576</td>
<td>1.13</td>
<td>1.15</td>
<td>2570</td>
<td>2522</td>
</tr>
<tr>
<td>200</td>
<td>2471</td>
<td>76</td>
<td>2547</td>
<td>1.23</td>
<td>1.24</td>
<td>2545</td>
<td>2469</td>
</tr>
<tr>
<td>300</td>
<td>2456</td>
<td>98</td>
<td>2534</td>
<td>1.27</td>
<td>1.28</td>
<td>2533</td>
<td>2455</td>
</tr>
<tr>
<td>400</td>
<td>2412</td>
<td>114</td>
<td>2526</td>
<td>1.30</td>
<td>1.30</td>
<td>2527</td>
<td>2413</td>
</tr>
<tr>
<td>500</td>
<td>2395</td>
<td>128</td>
<td>2523</td>
<td>1.31</td>
<td>1.31</td>
<td>2524</td>
<td>2396</td>
</tr>
<tr>
<td>600</td>
<td>2397</td>
<td>140</td>
<td>2519</td>
<td>1.32</td>
<td>1.32</td>
<td>2521</td>
<td>2381</td>
</tr>
</tbody>
</table>
4. **CONCLUSIONS.**

1. From relative measurements made by the hot wire method the thermal conductivity of hydrogen chloride has been found to be 1.61.

2. It has been found justifiable from experimental determinations to calculate the thermal conductivity of mixtures of chlorine with the following added gases, oxygen, nitrogen, hydrogen chloride, and carbon dioxide, between the compositions 33.3% chlorine / 66.7% added gas and 7.7% chlorine / 92.3% added gas, on the assumption that conductivity is a linear function of composition i.e. by the formula

\[ K = (K_M - K_{Cl_2}) [M]/ ([Cl_2] + [M]) + K_{Cl_2} \]
PART 3

THE HYDROGEN-CHLORINE REACTION
in
OXYGEN-FREE MIXTURES.
1. **HISTORICAL INTRODUCTION.**

The formation of hydrochloric acid by the action of light on a mixture of hydrogen and chlorine was first recorded by Cruickshank (42) in 1801. It was investigated, inter alios, by Seebeck, Gay-Lussac, Thenard, Favre and Silbermann. Draper (43) stated that the photochemical effect was roughly proportional to the light absorbed. The increase in pressure during illumination is named after him the "Draper Effect", though it is doubtful that he was truly the first observer of the same. Bunsen and Roscoe (44) between 1855 and 1859 repeated with greater accuracy the measurements showing the proportionality to the light absorbed.

A very large number of workers have investigated the problem in the last half century, and the accepted conclusions will be briefly summarized before considering in greater detail recent work.

The reaction is caused by light absorbed by chlorine.

There may be an "induction period" due to nitrogenuous and other impurities. From the point of view of this investigation these "inhibitors" are of note only as an experimental difficulty, and the action is instantaneous when complete purity of reactants is obtained.
The Einstein law is not even approximately obeyed. One quantum of light may bring about the union of $10^4 - 10^5$ molecules. A chain mechanism is thus involved.

The presence of oxygen leads to the formation of water, and, by breaking the reaction chains, reduces the quantum efficiency of HCl formation. Oxygen-rich systems are an entirely separate study in themselves, and the only importance of oxygen in the present work is that its addition slows down the reaction so much that the gas mixtures become, for practical purposes, insensitive to the light intensities used experimentally for oxygen-free mixtures. The amount of light of 3650 A.U. absorbed by a fixed amount of chlorine is unaltered by the presence of oxygen.

As in the case of the Budde effect in chlorine and bromine the necessity of the presence of traces of water vapour for reaction to take place has been postulated by some workers and denied by others. The results of Coehn and Jung (45) appear self-contradictory, suggesting the necessity of water vapour with light of the visible spectrum, and yet showing that in the ultra-violet region it plays no part.

Bodenstein and Bernreuther (46) have shown that water plays no part, and that the contradictory observations of other workers were due to the introduction of impurities in the processes of preparing and drying the reactants.
Seebeck (47) and Silbermann (48) stated that red rays were without action, while blue and violet rays gave rise to the reaction. W. Taylor (49) stated that no reaction occurs with light of wavelength greater than 4900 A.U., whilst Coehn and Jung (loc. cit.) calculated the limit as 5400 A.U. equivalent to 52.5 K. cals., and Weigert (50) gave it as 5900 A.U. Craggs and Allmand (loc. cit.) recorded that photocombination occurs at 5460 A.U., but not at 5790 A.U., while Bateman and Allmand (61) found that the quantum yield at 5400 A.U. was about 0.4 that at 4500 A.U. The decrease in efficiency began at approximately 5000 A.U., which corresponds roughly to the dissociation energy of the chlorine molecule. They showed that as the wavelength of the exciting light increases beyond the wavelength of the energy of dissociation, where the amount of energy which must be supplied by collision increases, the quantum yield drops rapidly. Bayliss (52) has recalculated the results of Craggs and Allmand, and arrives at the conclusion that the energy of activation is independent of wavelength. Dissociation does not end at the convergence limit but continues beyond it to about 5460 A.U., though here the dissociation is possibly not instantaneous, but may occur through the mechanism of an activated molecule colliding with another/
another molecule, the remainder of the energy required being derived from energy of collision.

Omitting the earlier mechanisms of reaction proposed and now discarded, we may commence with the scheme of Nernst (53) which had the form:

1. \( \text{Cl}_2 + \text{hv} \rightarrow \text{Cl}_2' \rightarrow 2\text{Cl} \)
2. \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)
3. \( \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \)
4. \( \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \)
5. \( \text{H} + \text{Cl} \rightarrow \text{HCl} \)
6. \( \text{H} + \text{H} \rightarrow \text{H}_2 \)

The exact form of reaction 1 was discussed in Part 1 and this need not be repeated here. It was shown from experiment that the probable form of reaction 4 is

\[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \]

\[ 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \]

where the first equation may or may not be reversible. Reactions 5 and 6 are highly exothermic (102 and 103 K. cals. approximately respectively), and can consequently not occur in simple form, but only at a wall or as a result of a three body collision.

We must consider the experimental data which has been published in direct support of the chain system

\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \]
\[ \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \]
\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \text{ etc.} \]
The formation of the initial centres of reaction is undoubtedly resultant on the action of light on the chlorine molecules, since the spectral region inducing the reaction is absorbed by these molecules, but not by hydrogen. Whether hydrogen plays an indirect part in the formation of the initial centres has been tested by Jost and Schweitzer. They exposed chlorine to illumination immediately before it was mixed with hydrogen to see whether the reaction could proceed in the dark. The chlorine was drawn at great speed through a tube exposed to illumination, while the light was prevented from entering the vessel where the gases mixed. A measurable reaction was found to take place provided the velocity of the gas was large, and that not more than $10^{-4}$ seconds elapsed between illumination and the mixing of the gases. The shortness of this interval was explained as follows. The centres, which originate in the chlorine on illumination, are destroyed on coming into contact with the walls of the tube. If diffusion alone were responsible for their reaching the walls, then their average life under the conditions of experiment would be about $6 \times 10^{-5}$ seconds, or about sixty times the observed value of $10^{-4}$. Owing to the large velocity of the gas and the existence of intense convection currents, the centres might be expected to reach the wall sooner, and the experimental values/
values were considered to conform to this explanation. It can therefore be assumed that the initial centres are originated from the action of light on the chlorine molecules, and that hydrogen does not take part in their formation.

Geib and Harteck (55) have proved experimentally the formation of hydrogen atoms in the course of the reaction. A weak stream of chlorine was passed through a narrow capillary into the vessel containing hydrogen. The illumination was very intense, and the whole mass of chlorine combined into hydrogen-chloride at the very mouth of the capillary. Thus for lack of a partner molecule of chlorine, the hydrogen atoms set free during the development of the chains could only recombine to molecular hydrogen. The latter process is very slow, requiring either a collision at the walls, or a three body collision

\[ H + H + M \rightarrow H_2 + M \]

in the gaseous phase.

The collision of a hydrogen atom with a para-hydrogen molecule results in the formation of ortho-hydrogen. At room temperature one encounter out of 2 millions leads to the reaction:

\[ H_2^\text{para} + H \rightarrow H + H_2^\text{ortho} \]

Geib and Harteck showed that in the process of HCl formation/
formation para-hydrogen actually changes to ortho-
hydrogen, and calculations showed that concentrations
of from $0.3 \times 10^{-5}$ to $4.7 \times 10^{-5}$ mm. of hydrogen atoms
were involved. Thus the formation of hydrogen atoms
during the chain reaction is amply proved. The
formation of chlorine atoms in the secondary stage
$$H + Cl_2 \rightarrow HCl + Cl$$
cannot be directly proved experimentally, but no
reasonable doubt can be cast upon it.

The experimental methods by which the
photo-combination of hydrogen and chlorine may be
studied have been limited by the fact that no permanent
change of pressure accompanies the reaction in a vessel
of constant volume, and while a small decrease in
pressure takes place in mixtures containing oxygen,
this change is so small that it does not appreciably
alter the concentration of oxygen. Bunsen and Roscoe
(loc. cit.) developed the water actinometer method
in which by addition of a sufficient quantity of
liquid water to the reaction vessel, the hydrogen chloride
formed is removed, and the progress of the reaction can
then be studied by the change in volume at constant
pressure. This method suffers from several disadvantages.
The action of HCl on the reaction velocity cannot be
studied as it is removed as formed, and the conclusions
arrived at will therefore only be exactly true under
conditions/
conditions where the product HCl can be entirely ignored i.e. only at the very commencement of the reaction. The presence of water is a great disadvantage. It is impossible to obtain a wall which is not water saturated; chlorine itself is very appreciably soluble so that the concentration of reactants is almost certainly only approximately known; reaction might occur between the illuminated chlorine and the water vapour; and there is great danger of introducing inhibitors to the reaction with the water. In recent times this method has however been used by Chapman and his co-workers (56).

Bodenstein and Dux (57) introduced the method of freezing out the chlorine and hydrogen chloride, which is free from the objections raised against the water actinometer, but is open to the objection that at high pressure complete freezing out is not attained with certainty in the presence of an inert gas nor even of much hydrogen itself, while the original concentrations of the reactants may not be effectively regained before the experiment is resumed, owing to difficulties of mixing and slowness of diffusion.

To overcome the shortcomings of previous methods, a new method was applied by Ritchie and Norrish (loc. cit.) which involved no addition to, or disturbance/
disturbance of the reaction system, and it is this method which is made use of in the following work. It consisted in determining the extent of reaction at any time from the relative amount of light which was transmitted by the residual chlorine. The graphic relationship between chlorine pressure and \( \log_{10} \frac{I}{I_0} \), where \( I_0 \) represents the transmitted light when the chlorine pressure is zero, and \( I \) that transmitted by chlorine at any other pressure, is represented by a straight line passing through the origin. In mixtures where the reaction was suitably slow the chlorine concentration was determined continuously throughout the period of illumination, and the rate of reaction was then calculated from the slope of the resultant curve showing the relationship between the pressure of chlorine and the time of illumination. This was called the "graphical method". On the other hand, when the reaction velocity was too high, or the intensity used too low to permit of accurate measurement this way, the concentration of chlorine after a given exposure was determined with full intensity light after an excess of oxygen had been added to render the mixture insensitive. Calculation was then performed on the assumption that the changes in concentration of the reactants, and in the intensity of the light absorbed, were linear over the range.
This procedure was called the "method of averaging".

The disadvantages of the earlier methods, have in the past played so great a part in obscuring the exact nature of the various factors controlling the rate of reaction, that it has been thought advisable to give this summary here rather than postpone it to the description of experimental method.

Bodenstein and Unger (58) stated that the rate of the hydrogen chlorine reaction in the oxygen free mixtures of their experiments was proportional to the first power of the absorbed light; while Chapman and Gibbs (69) found a rate nearly proportional to the square root of the intensity. Ritchie and Norrish (loc. cit.) found that the quantum efficiency over a wide range of conditions was given by the formula:

\[
\gamma = \frac{2.8 \times 10^5 [H_2] [Cl_2]}{[Cl_2] + 1.7 [HCl] (I_{abs})^{0.4}}
\]

Their scheme of reaction was:

1. \( Cl_2 + h\nu \rightarrow Cl + Cl \) \( k_1 \)
2. \( Cl + H_2 \rightarrow HCl + H (5.8 \text{ K. cals.}) \) \( k_2 \)
3. \( H + Cl_2 \rightarrow HCl + Cl (44.8 \text{ " " }) \) \( k_3 \)
4. \( H + HCl \rightarrow H_2 + Cl (0.8 \text{ " " }) \) \( k_4 \)
5. \( Cl + Cl \rightarrow Cl_2 (57.4 \text{ " " }) \) \( k_5 \)

which/
which gives the formula: 

\[
\gamma = \frac{2 k_2 k_3 \sqrt{\frac{k_1}{k_5}} [H_2] [Cl_2]}{(k_3 [Cl_2] + k_4 [HCl]) (I_{abs})^{0.5}}
\]

which agrees with the empirical equation except that the power of the intensity is 0.5 instead of 0.6.

They first recorded the retarding effect of HCl in the photo-chemical reaction, which they ascribed entirely to reaction 4, a conclusion which now appears to be inadequate. Christiansen (60) had already recorded this retarding effect in the thermal reaction of hydrogen and chlorine.

Allmand with his co-workers Craggs and Squire (loc.cit.) have investigated the hydrogen chlorine reaction, mainly under conditions of very low pressure of hydrogen. They found the intensity exponent of the rate of HCl formation to vary between the limits 1 and 0.05, becoming less the higher the chlorine pressure and the higher the incident intensity. As the pressure of chlorine was increased at constant intensity, the rate of reaction was found to pass through a maximum and then decline.

For the conditions under which an relationship was observed they proposed the mechanism 1.
1. \( \text{Cl}_2 + \text{H}_2 \rightarrow 2\text{Cl} \)

2. \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)

3. \( \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \)

4. \( \text{Cl} + \text{Cl}_2 \rightarrow \text{Cl}_3 \)

5. \( \text{Cl}_3 \rightarrow \text{Cl} + \text{Cl}_2 \)

6. \( 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \)

from which they derived the kinetic expression

\[
y_{(\text{H}_2)} = \frac{k_2 [\text{H}_2]}{k_7 [\text{Cl}_2]} (k_6 \cdot I_{a,b})^{0.5}
\]

They considered that \( \text{HCl} \) under varying conditions both accelerates and retards the reaction. They found that intensive drying of the hydrogen and chlorine does not inhibit the reaction. On the contrary, the addition of small quantities of water vapour to dried gases retarded the reaction somewhat, which they suggested was due to a surface carrying adsorbed water having a greater efficiency in removing chain carriers.

Potts and Rollefson (loc. cit.) found that at temperatures below 172° K the rate of reaction was proportional to the square root of the intensity, but under other conditions they were in general agreement with the results of Bodenstein and Unger (loc. cit.)

M. Tamura (61) found that the rate of formation of \( \text{HCl/} \)
HCl was proportional to $I_{abs}$ in confirmation of the results of Ritchie and Norrish. He considered that chains were terminated chiefly by self neutralization, but concluded that the mechanism involved was not the simple triple collision

$$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$$
2. **THEORETICAL DISCUSSION.**

We shall adopt here the method of first setting out the reactions which appear fairly well proven, and then give consideration to the various additional reactions which may, or may not, take place, without attempting at this stage to derive any kinetic expression. Later, after the statement of the experimental results, and the analysis of the tendencies shown therein, we shall consider what equation best satisfies these new results, and, in conjunction with the conclusions of previous workers, attempt to formulate a consistent mechanism.

The initial dissociation and the Nernst chain are now well established:

1. \( \text{Cl}_2 + h\gamma \rightarrow \text{Cl} + \text{Cl} \)
2. \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)
3. \( \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \).

It would appear from Part I of this work that the recombination of chlorine atoms in the gas phase occurs in the form:

4. \( \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \)
5. \( 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \).

There is every indication that under suitable conditions chlorine atoms recombine at the surface of the vessel:

6. \( \text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2 \) at surface.
It is possible that the $\text{Cl}_3$ molecule may dissociate to some extent in the gas phase, though this possibility rests not on any proof, but on a lack of disproof.

$$\text{Cl}_3 \rightarrow \text{Cl} + \text{Cl}_2 \text{ (with or without third body)}.$$ 

It is uncertain whether the magnitude of the third body action of HCl, as found in the examination of the photo-expansion of chlorine, is sufficient to explain the whole of the retarding action of HCl in the hydrogen-chlorane reaction observed by Ritchie and Norrish, and thus while their suggestion that equation 2 is reversible has been strongly attacked by Potts and Rollefson (62) and by Bodensteinn and Winter (63), it does not appear justifiable to exclude altogether from consideration the possibility of some such reaction as:

$$\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$$

If as would appear possible HCl has some other effect on the reaction besides the role of stabilizer in the three body collision (reaction 4), then the reversal of equation 2 seems definitely the most probable. It has a heat evolution of about 0.8 K.Cals., whereas a reversal of reaction 3 would require 44.8 K.Cals. as energy of activation. In addition it may be pointed out that Schwab (64) has shown that HCl does not react with atomic chlorine, whilst Rodebush and Spielman (34) have found that the reaction $\text{HCl} + \text{H} \rightarrow \text{H}_2 + \text{Cl}$ does take place under suitable conditions.
conditions, Craggs, Squire and Allmand, in their examination of the retarding effect of HCl, expressed the opinion that, of the retardation of 20-30% observed by them, only 2-3% could be attributed to this reaction. The remainder of the effect they ascribed entirely to third body efficiency.

One might also suggest the reaction:

$$\text{Cl}_3 + \text{HCl} \rightarrow \text{H} + 2\text{Cl}_2$$

but this is no more than the result of combining the equations:

$$\text{Cl}_3 + \text{M} \rightarrow \text{Cl} + \text{Cl}_2 + \text{M}$$
$$\text{Cl} + \text{HCl} \rightarrow \text{H} + 2\text{Cl}_2$$

where M is limited to the special case HCl. These two have been considered separately already.

There are three other possible reactions of the Cl$_3$ molecule. It may be adsorbed on the surface of the wall and there destroyed.

$$\text{Cl}_3 \rightarrow \text{surface}.$$  

It may also react in the gas phase with a chlorine atom:

$$\text{Cl}_3 + \text{Cl} \rightarrow 2\text{Cl}_2$$

but as stated in Part 1 it is considered by Allmand that this reaction is unimportant except at low pressures of chlorine.

Thirdly, Cl$_3$ may react with hydrogen:

$$\text{Cl}_3 + \text{H}_2 \rightarrow \text{HCl} + \text{Cl}_2 + \text{H}$$

but this would give rise to terms in (H$_2$)$^a$ in the kinetic/
kinetic expression, and make $\gamma \propto (H_2)^n$ where $n > 1$
which has never been observed. Further, Craggs and
Allmand considered that the efficiency of the Cl$_3$-$H_2$
collision is considerably less than that of the Cl-$H_2$
collision. Kimball and Hyring (65) gave the ratio
of efficiencies as $10^{-3} - 10^{-4}$, whilst according to
Rollefson (66) it is $10^{-1} - 10^{-2}$.

A summary may conveniently be made:

1. Cl$_2$ + h$\nu$ $\rightarrow$ Cl + Cl
2. Cl + H$_2$ $\rightarrow$ HCl + H
3. H + Cl$_2$ $\rightarrow$ HCl + Cl
4. Cl + Cl$_2$ + M $\rightarrow$ Cl$_3$ + M
5. 2Cl$_3$ $\rightarrow$ 3Cl$_2$
6. Cl $\rightarrow$ \frac{1}{2}Cl$_2$ at surface.

It would appear that the above must form part of any
scheme of reaction.

The following reactions have varying prob-
ability.

H + HCl $\rightarrow$ H$_2$ + Cl certainly takes
place, but it is uncertain whether it attains a
magnitude to make it really important.

Cl$_3$ $\rightarrow$ Cl$_2$ + Cl (whether spontaneously or
after collision).

No experimental data in support of such a reaction
is known, though it cannot be excluded from
consideration.

Cl$_3$ $\rightarrow$ destruction at surface.

According to Allmand Cl$_3$ is more readily adsorbed
than/
than the chlorine atom. To what extent it is decomposed when desorbed is not known.

\[ \text{Cl}_3 + \text{Cl} \rightarrow 2\text{Cl}_2 \]

Important only at low pressures of chlorine.

\[ \text{Cl}_3 + \text{H}_2 \rightarrow \text{HCl} + \text{Cl}_2 + \text{H} \]

This requires \( \gamma \propto (\text{H}_2)^n \) where \( n > 1 \), which is contrary to all existing observations.
3. **DESCRIPTION OF APPARATUS.**

The apparatus used in the hydrogen-chlorine experiments was the same as that used in measuring the photo-expansion of chlorine (Figure 1), with the following modifications. In the purification of hydrogen the copper catalyst was renewed and the platinum filament catalyst replaced by a tube filled with palladiumised asbestos maintained at 300°C by a heating coil. Two phosphorus pentoxide tubes were used, one after each catalyst. The mercury pump system was not included.

The soft glass reaction flask was replaced by a cylindrical quartz vessel with plane-end faces, of volume 31.34 c.c. Connection was made to the main apparatus by a ground glass joint. The reaction vessel was immersed in water at constant temperature, maintained by the circulating water system, and contained in a metal bath with lid, entirely painted black, and fitted with two thin glass windows on opposite sides.

The light source was a quartz mercury vapour lamp, rated at 100 volts D.C., but run most steadily at about 70 volts from a 100 volts D.C. system, derived from large capacity accumulators which gave a steady voltage. No readings here recorded were made during, or immediately after, the charging of the accumulators, nor/
nor when they were excessively discharged. The voltage was controlled by rheostats specially intended to maintain constant resistance under heavy load.

The lamp was enclosed in a wooden box with a small circular aperture level with the central region of the arc. The light was passed successively through a Chance's ultra-violet glass, a focussing lens consisting of a spherical 500 c.c. flask filled with a solution containing 4.4 gm. CuSO₄·5H₂O and 150 c.c. ammonia 0.8 s.g. in 1 litre, and 3 blue glass plates to reduce the intensity to a suitable value. Finally a second circular aperture was placed in front of the window through which the light beam entered, so that only the central portion of the beam was admitted. Practically all the reaction vessel volume was then illuminated. The light emerging from the other window was focussed by a quartz lens on to the photronic cell, which was contained in a black wooden box with a circular aperture in immediate contact with the second window. A movable shutter in a wooden frame was placed between the focussing flask and the blue glass plates to obscure the light as required. The whole light and reaction system was draped in black cloth, while the tubing leading from tap t7 to the reaction vessel and the Bourdon gauge was bound with black insulating tape. The Bourdon gauge was/
was also screened from light. A test was carried out to show that any residual light had no appreciable action on a mixture of 50 mm. Cl₂ and 50 mm. H₂, during at least 10 times the maximum time elapsing, during experiments, between the admission of an active mixture to the reaction vessel and the inhibition of further appreciable action by the addition of oxygen.

When it was required to reduce the intensity during any particular experiment, a half-tone light filter was clamped in the path of the light between the Chance's ultra-violet plate and the focusing flask. Every reading in such experiments was made with and without the filter, and it was found, that over the whole range of readings, the filter reduced the intensity by a constant factor within the attainable accuracy of measurement.

Chlorine and oxygen were prepared and purified as in Part 1 of this work. Hydrogen was again prepared by the electrolysis of an aqueous solution of KOH and baryta, and was purified from oxygen by the two catalysts described above. HCl was in every case obtained by photosynthesis within the reaction vessel from the normal hydrogen and chlorine.

Apiezon M grease was used on the taps, and was thoroughly chlorinated with illumination, when it hardened somewhat and did not inhibit the reaction.
Draper effects were sharp in every case. The minimum quantity of tap grease was used and the bore of the taps was kept completely free.

Pressures were read to a tenth of a millimetre with a probable error of ± 0.1 mm. The intensities were read as scale readings of the spot light of the mirror galvanometer. The total intensities were of the order of 27.0 scale divisions (full) and 7.0 (reduced), with $I_{abs}$ 13.0 and 3.3, with a possible error of ± 0.1 divisions. In experiments with intensities reduced by the half-tone filter, the experimental error was reduced by calculating all reduced values from the equivalent full value, by applying the mean observed constant for the filter (0.2778) to the full intensity value, so keeping the error to the equivalent of ± 0.1 divisions in 12 divisions for $I_{abs}$ or in 27 divisions for $I_0$. 
4. **EXPERIMENTAL PROCEDURE AND RESULTS.**

The apparatus was first thoroughly evacuated by the Hyvac oil pump for some considerable time. Before the first experiment each day the windows of the bath and the end faces of the reaction vessel were washed with alcohol and then water. The water-alcohol mixture was removed completely from the bath by suction, and the bath allowed to fill up again in the normal way. The alignment and focussing of the light beam was checked and the light-proof coverings replaced. The above procedure thus described was performed once per day; the sequel holds for every series of readings in so far as it is appropriate.

The intensity of the light was measured by the galvanometer deflection. The high vacuum line, gauge, and reaction vessel were washed out with chlorine, the vessel being illuminated during this process. The system was evacuated once more and the intensity again determined. The requisite pressure of chlorine was admitted and the system illuminated for 10 minutes, during which the intensity transmitted was observed and recorded. For experiments where neither oxygen nor HCl were required in the initial mixture the required pressure of hydrogen was now added. For the exposure the shutter was drawn back quickly while watching the pointer.
pointer of the Bourdon gauge, since the sharpness and magnitude of the Draper effect forms a reliable immediate indication of the purity of the reactants and the absence of inhibitors. At the end of the required exposure the shutter was moved back. Large excess of oxygen (say 260 mm.) was now quickly added to the gas mixture. The intensity transmitted was again determined. The vessel was then evacuated and the total intensity of the light measured again.

For the purpose of calibrating the system, experiments with starting mixtures of 50 mm. Cl₂ / 50 mm. O₂ / 50 mm. H₂ were performed at intervals between other series, and the absolute quantum efficiencies calculated by the formula of Norrish and Ritchie:

\[ \gamma_{HCl} = \frac{3.77 \times 10^4 [H_2][Cl_2]}{9.25 [O_2][Cl_2] + 1.7 [HCl] + [O_2][H_2][H_2] + 4 [HCl] + 140} \]

Relative quantum efficiencies were in all cases calculated by the formula:

\[ \gamma'_{HCl} = \frac{\Delta [HCl]}{t I_{abs}} \] (relative)

and were subsequently converted to absolute values by multiplying by the constant k where

\[ \gamma_{HCl}^{\text{absolute}} = k \gamma'_{HCl} = k \frac{\Delta [HCl]}{t I_{abs}} \] (absolute)

This method assumes that \( \gamma \) is independent of the volume of
of the reaction vessel, and the formula is based on experiments with 4060 A.U. light. However the method was found satisfactory by Ritchie in subsequent work in oxygen rich mixtures (27). He also used the formula for 3650 A.U. light instead of 4060 A.U., and his vessel of approximate capacity of 35 c.c. was even larger than that here used (31.34), while neither are very different from the vessel of 25.4 c.c. for which the formula was obtained. It may be said that conditions here differ little from those of Norrish and Ritchie, and further it is only the order of magnitude of the absolute quantum efficiency which is required for our present purpose. The procedure for oxygen rich experiments was the same as the above, up to the measurement of the residual intensity after the admission and illumination of chlorine. Oxygen was now added and the intensity again measured after 5 minutes illumination of the mixture. Hydrogen was then added. The shutter having been drawn back the galvanometer pointer was read every 10 seconds. The mean of all readings in the \((x + 1)\) minute was taken as the true value at \(x\) minutes 30 seconds. It was in practice found that such mixtures, under the conditions of experiment, had reacted to the desired amount after about 20 minutes illumination, and accordingly 19 minutes 30 seconds was taken as the exposure in each such/
such series. The best value for this time was found by plotting intensity values against time from 14 minutes 30 seconds to 24 minutes 30 seconds. After evacuation the total intensity was redetermined.

For all experiments where an initial concentration of HCl was desired, chlorine was added equivalent to both the chlorine and HCl required, after which sufficient hydrogen was added to form the necessary HCl. The mixture was illuminated for 60-90 minutes, after which the residual chlorine was determined by means of the intensity transmitted. The additional hydrogen required for the reacting mixture was now added, and the remaining procedure was as already described above.

As already partially stated in the historical introduction the measurement of unknown chlorine concentration depended on the application of Beer's Law:

\[
\log_{10} \frac{I_0}{I} = \text{constant} \times (\text{Cl}_2)
\]

where \(I_0\) is the total intensity transmitted by the system when the reaction vessel is evacuated, and \(I\) the residual intensity unabsorbed by a concentration of chlorine \((\text{Cl}_2)\). It was found most convenient in such calculations to determine the best value for the Beer's Law constant from the mean of as many determinations as possible (40 readings with chlorine varying from 35 mm. to 100 mm. were actually made use of), and then to use this value in all subsequent calculations. The mean value/
value so determined was 0.00593. The value for $I_{50 \text{ mm. } Cl_2}$ (or other known initial concentration as the case may be) is now obtained, and can be used to determine a calculated value for $I_0$ at that moment, which forms an additional check on the constancy of this magnitude, which (at least in the form of apparatus here used) is only directly observable at the beginning and end of a "run" and not intermediately.

The value for $I_{abs}$ required in calculations of the quantum efficiency of HCl formation, is the difference between the constant $I_0$ and the mean value for $I_{xCl_2}$ (where $I_{xCl_2}$ is the intensity transmitted by a gas mixture containing an unknown pressure of chlorine $xCl_2$). The method by which $I_{xCl_2}$ was determined was to take the value of $xCl_2$ when half the reaction which takes place during the exposure had occurred, and calculate from this a value for $I_{xCl_2}$ i.e., antilog $(\log_{10} I_0/0.00593 \times (Cl_2))$. This is perhaps more exact than taking the arithmetic mean of $I_{xCl_2}$ at the beginning and end of the exposure, though the values obtained by the two methods differ only by a small and almost constant amount.

The calculated concentration of chlorine after all exposures, and also the calculated initial chlorine concentration for HCl rich mixtures was found by the formula:

$$(Cl_2) = \frac{(\log_{10} I_0/I)}{0.00593}.$$
**RESULTS.**

Calibration of the system.

The following results were obtained with gas mixtures of initial approximate composition of 50 mm. Cl₂ / 50 mm. H₂ / 50 mm. O₂. The serial number, here as later, denotes the order in which all experiments were performed.

γ, γ' and κ, and their methods of calculation, have been already defined.
From Table 20 the mean value for $k$ is approximately $6.4 \times 10^{-4}$. This value will be used in all later calculations. As the result of any particular experiment may be made use of to illustrate more than one tendency, it is considered most convenient to first give a table of all oxygen-free results, and then to arrange them in separate tables to illustrate the various tendencies shown by them. All relevant data is given in the main table; while the comparison can then be reduced to a very simple form, since any further information about the series can always be obtained by reference back to the main table. As it seems well established that the quantum efficiency is proportional to the pressure of hydrogen, all results will be given corrected to 40 mm. $H_2$ on this assumption in tables of comparison.
<table>
<thead>
<tr>
<th>Serial Number</th>
<th>I&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Time (secs.)</th>
<th>Cl&lt;sub&gt;2&lt;/sub&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>HCl</th>
<th>ΔHCl</th>
<th>I&lt;sub&gt;abs&lt;/sub&gt;</th>
<th>10&lt;sup&gt;4&lt;/sup&gt;&lt;sub&gt;γ, x&lt;/sub&gt;</th>
<th>γ</th>
<th>γ&lt;sub&gt;H&lt;sub&gt;2&lt;/sub&gt;=40&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>7.2</td>
<td>50.0</td>
<td>44.61</td>
<td>40.61</td>
<td>14.77</td>
<td>14.77</td>
<td>3.31</td>
<td>1735</td>
<td>11270</td>
<td>11090</td>
</tr>
<tr>
<td>32</td>
<td>25.5</td>
<td>25.0</td>
<td>41.38</td>
<td>37.33</td>
<td>21.23</td>
<td>21.23</td>
<td>11.08</td>
<td>1538</td>
<td>9690</td>
<td>10390</td>
</tr>
<tr>
<td>33</td>
<td>26.55</td>
<td>15.0</td>
<td>45.1</td>
<td>41.1</td>
<td>13.7</td>
<td>13.7</td>
<td>12.29</td>
<td>1488</td>
<td>9370</td>
<td>9120</td>
</tr>
<tr>
<td>34</td>
<td>7.43</td>
<td>35.6</td>
<td>46.3</td>
<td>42.3</td>
<td>11.4</td>
<td>11.4</td>
<td>3.50</td>
<td>1830</td>
<td>11530</td>
<td>110900</td>
</tr>
<tr>
<td>35</td>
<td>25.25</td>
<td>15.5</td>
<td>45.1</td>
<td>41.1</td>
<td>13.8</td>
<td>13.8</td>
<td>11.69</td>
<td>1523</td>
<td>9600</td>
<td>9345</td>
</tr>
<tr>
<td>36</td>
<td>7.3</td>
<td>49.7</td>
<td>43.65</td>
<td>45.35</td>
<td>16.3</td>
<td>16.3</td>
<td>3.304</td>
<td>1988</td>
<td>12520</td>
<td>11930</td>
</tr>
<tr>
<td>38</td>
<td>30.35</td>
<td>18.0</td>
<td>36.3</td>
<td>59.8</td>
<td>31.4</td>
<td>31.4</td>
<td>11.95</td>
<td>2920</td>
<td>18400</td>
<td>12310</td>
</tr>
<tr>
<td>40</td>
<td>26.55</td>
<td>38.0</td>
<td>33.2</td>
<td>33.9</td>
<td>128.9</td>
<td>21.6</td>
<td>10.85</td>
<td>1075</td>
<td>6770</td>
<td>7990</td>
</tr>
<tr>
<td>41</td>
<td>27.75</td>
<td>16.0</td>
<td>44.22</td>
<td>40.92</td>
<td>15.55</td>
<td>15.55</td>
<td>12.64</td>
<td>1539</td>
<td>9695</td>
<td>9480</td>
</tr>
<tr>
<td>42</td>
<td>26.8</td>
<td>31.0</td>
<td>37.15</td>
<td>36.15</td>
<td>126.9</td>
<td>16.9</td>
<td>10.73</td>
<td>1014</td>
<td>6390</td>
<td>7080</td>
</tr>
<tr>
<td>45</td>
<td>27.0</td>
<td>21.6</td>
<td>28.27</td>
<td>42.47</td>
<td>16.25</td>
<td>16.25</td>
<td>3.66</td>
<td>1733</td>
<td>10980</td>
<td>10320</td>
</tr>
<tr>
<td>46</td>
<td>25.45</td>
<td>16.0</td>
<td>59.1</td>
<td>38.5</td>
<td>17.4</td>
<td>17.4</td>
<td>14.74</td>
<td>1473</td>
<td>9310</td>
<td>9630</td>
</tr>
<tr>
<td>47</td>
<td>26.65</td>
<td>15.0</td>
<td>45.0</td>
<td>41.0</td>
<td>14.0</td>
<td>14.0</td>
<td>12.31</td>
<td>1517</td>
<td>9550</td>
<td>9320</td>
</tr>
<tr>
<td>56</td>
<td>3.37</td>
<td>41.0</td>
<td>50.6</td>
<td>44.8</td>
<td>107.0</td>
<td>13.2</td>
<td>4.2</td>
<td>1532</td>
<td>9660</td>
<td>8620</td>
</tr>
<tr>
<td>57</td>
<td>8.05</td>
<td>62.4</td>
<td>47.0</td>
<td>38.8</td>
<td>114.0</td>
<td>14.8</td>
<td>3.845</td>
<td>1233</td>
<td>7730</td>
<td>8020</td>
</tr>
<tr>
<td>58</td>
<td>29.8</td>
<td>50.5</td>
<td>43.81</td>
<td>35.31120.38</td>
<td>21.13</td>
<td>13.5</td>
<td>1023</td>
<td>6470</td>
<td>7240</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>8.2</td>
<td>60.6</td>
<td>45.85</td>
<td>37.65116.3</td>
<td>14.1</td>
<td>3.843</td>
<td>1210</td>
<td>7630</td>
<td>8060</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>29.0</td>
<td>62.0</td>
<td>41.56</td>
<td>31.46226.6</td>
<td>17.08</td>
<td>12.65</td>
<td>397</td>
<td>2502</td>
<td>3186</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>30.75</td>
<td>15.5</td>
<td>43.4</td>
<td>39.2</td>
<td>17.3</td>
<td>17.3</td>
<td>13.34</td>
<td>1601</td>
<td>10100</td>
<td>10300</td>
</tr>
<tr>
<td>62</td>
<td>30.3</td>
<td>47.7</td>
<td>37.9</td>
<td>65.2</td>
<td>227.6</td>
<td>29.2</td>
<td>12.52</td>
<td>978</td>
<td>6160</td>
<td>3730</td>
</tr>
<tr>
<td>63</td>
<td>30.3</td>
<td>55.0</td>
<td>40.75</td>
<td>31.05227.8</td>
<td>16.7</td>
<td>13.02</td>
<td>442</td>
<td>2735</td>
<td>3590</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>3.31</td>
<td>115.6</td>
<td>40.35</td>
<td>33.05226.3</td>
<td>11.9</td>
<td>3.54</td>
<td>522</td>
<td>3668</td>
<td>4445</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>8.50</td>
<td>75.0</td>
<td>38.2</td>
<td>37.9</td>
<td>235.5</td>
<td>17.2</td>
<td>3.4</td>
<td>569</td>
<td>3535</td>
<td>3790</td>
</tr>
<tr>
<td>72</td>
<td>29.6</td>
<td>40.1</td>
<td>23.4</td>
<td>37.35</td>
<td>126.25</td>
<td>14.5</td>
<td>8.16</td>
<td>886</td>
<td>5590</td>
<td>5995</td>
</tr>
<tr>
<td>73</td>
<td>29.5</td>
<td>41.5</td>
<td>23.2</td>
<td>35.55</td>
<td>126.45</td>
<td>14.3</td>
<td>8.07</td>
<td>855</td>
<td>5395</td>
<td>6070</td>
</tr>
</tbody>
</table>
Variation of quantum efficiency with increasing chlorine concentration (HCl concentration about 15 mm.)

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Cl₂</th>
<th>HCl</th>
<th>I_{abs}</th>
<th>H₂ = 40 mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>28.27</td>
<td>16.25</td>
<td>8.56</td>
<td>10320</td>
</tr>
<tr>
<td>38</td>
<td>36.30</td>
<td>31.40</td>
<td>11.95</td>
<td>13310</td>
</tr>
<tr>
<td>32</td>
<td>41.38</td>
<td>21.23</td>
<td>11.08</td>
<td>10390</td>
</tr>
<tr>
<td>61</td>
<td>45.4</td>
<td>17.3</td>
<td>13.84</td>
<td>10300</td>
</tr>
<tr>
<td>41</td>
<td>44.2</td>
<td>15.55</td>
<td>12.64</td>
<td>9480</td>
</tr>
<tr>
<td>47</td>
<td>45.0</td>
<td>14.0</td>
<td>12.31</td>
<td>9320</td>
</tr>
<tr>
<td>35</td>
<td>45.1</td>
<td>13.8</td>
<td>11.69</td>
<td>9345</td>
</tr>
<tr>
<td>33</td>
<td>45.1</td>
<td>13.7</td>
<td>12.29</td>
<td>9120</td>
</tr>
<tr>
<td>46</td>
<td>59.1</td>
<td>17.4</td>
<td>14.74</td>
<td>9680</td>
</tr>
</tbody>
</table>

From Table 22 it will be seen that the quantum efficiency rises to a maximum where the pressure of chlorine is about 36 mm., and then steadily declines.
Variation of quantum efficiency with increasing chlorine concentration (HCl pressure approximately 125 mm.).

**Table 23.**

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Cl₂</th>
<th>HCl</th>
<th>T abs</th>
<th>H₂ = 40 mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>23.2</td>
<td>126.45</td>
<td>8.07</td>
<td>5995</td>
</tr>
<tr>
<td>72</td>
<td>23.4</td>
<td>126.25</td>
<td>8.16</td>
<td>6070</td>
</tr>
<tr>
<td>42</td>
<td>37.15</td>
<td>126.9</td>
<td>10.73</td>
<td>7680</td>
</tr>
<tr>
<td>40</td>
<td>38.2</td>
<td>128.9</td>
<td>10.85</td>
<td>9480</td>
</tr>
<tr>
<td>58</td>
<td>43.81</td>
<td>130.38</td>
<td>13.5</td>
<td>7240</td>
</tr>
</tbody>
</table>

From Table 23 it will be seen that the quantum efficiency rises to a maximum somewhere in the region Cl₂ = 38 mm., and subsequently declines.
Variation of quantum efficiency with increasing chlorine pressure (HCl concentration approximately 225 mm.).

**TABLE 24.**

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Cl₂</th>
<th>HCl</th>
<th>Iₐₙ₀s</th>
<th>H₂=40 mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>37.9</td>
<td>227.6</td>
<td>12.52</td>
<td>3780</td>
</tr>
<tr>
<td>63</td>
<td>40.75</td>
<td>227.8</td>
<td>13.02</td>
<td>3590</td>
</tr>
<tr>
<td>60</td>
<td>41.56</td>
<td>226.6</td>
<td>12.65</td>
<td>3186</td>
</tr>
</tbody>
</table>

From Table 24 it will be that the quantum efficiency declines as the chlorine concentration rises from 37.9 mm. to 41.56 mm., but no data is available outside this region.

From the last three tables it appears, that under these conditions of experiment, where the pressure of HCl is in the region 15 mm. or 125 mm. the quantum efficiency rises as the pressure of chlorine is increased to about 37 mm.; whilst above 38 mm. in all the experiments carried out it declines with increased pressure of chlorine.
Variation of quantum efficiency with increasing concentration of HCl.

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Cl₂</th>
<th>HCl</th>
<th>I_{abs}</th>
<th>H₂ = 40 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Intensity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>36.3</td>
<td>31.4</td>
<td>11.95</td>
<td>12310</td>
</tr>
<tr>
<td>32</td>
<td>41.58</td>
<td>21.23</td>
<td>11.08</td>
<td>10390</td>
</tr>
<tr>
<td>61</td>
<td>43.4</td>
<td>17.3</td>
<td>13.84</td>
<td>10300</td>
</tr>
<tr>
<td>41</td>
<td>44.22</td>
<td>15.55</td>
<td>12.64</td>
<td>9480</td>
</tr>
<tr>
<td></td>
<td>37.15</td>
<td>126.9</td>
<td>10.73</td>
<td>7080</td>
</tr>
<tr>
<td></td>
<td>38.2</td>
<td>128.9</td>
<td>10.85</td>
<td>7990</td>
</tr>
<tr>
<td></td>
<td>43.81</td>
<td>120.38</td>
<td>13.5</td>
<td>7240</td>
</tr>
<tr>
<td></td>
<td>37.9</td>
<td>227.6</td>
<td>12.52</td>
<td>3780</td>
</tr>
<tr>
<td></td>
<td>40.75</td>
<td>227.8</td>
<td>13.02</td>
<td>3590</td>
</tr>
<tr>
<td></td>
<td>41.56</td>
<td>226.6</td>
<td>12.65</td>
<td>3186</td>
</tr>
<tr>
<td>Reduced Intensity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>43.85</td>
<td>16.3</td>
<td>3.304</td>
<td>10930</td>
</tr>
<tr>
<td>30</td>
<td>44.61</td>
<td>14.77</td>
<td>3.31</td>
<td>11090</td>
</tr>
<tr>
<td>34</td>
<td>46.3</td>
<td>11.4</td>
<td>3.50</td>
<td>10900</td>
</tr>
<tr>
<td></td>
<td>45.85</td>
<td>116.3</td>
<td>3.843</td>
<td>8060</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>114.0</td>
<td>3.845</td>
<td>8020</td>
</tr>
<tr>
<td></td>
<td>50.6</td>
<td>107.0</td>
<td>4.2</td>
<td>8620</td>
</tr>
<tr>
<td></td>
<td>58.2</td>
<td>235.6</td>
<td>3.4</td>
<td>3790</td>
</tr>
<tr>
<td></td>
<td>40.35</td>
<td>226.8</td>
<td>3.54</td>
<td>4445</td>
</tr>
</tbody>
</table>
From Table 25 we may interpolate a set of results for the conditions $(\text{Cl}_2 = 40 \text{ mm}.; \text{H}_2 = 40 \text{ mm}.)$ for both full and reduced intensity, and for the three ranges of HCl pressure studied.

**TABLE 26**

<table>
<thead>
<tr>
<th>HCl Pressure (mm)</th>
<th>Quantum Efficiency (Full Intensity)</th>
<th>Quantum Efficiency (Reduced Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>10500</td>
<td>11000</td>
</tr>
<tr>
<td>125</td>
<td>7500</td>
<td>8000</td>
</tr>
<tr>
<td>225</td>
<td>3650</td>
<td>4400</td>
</tr>
</tbody>
</table>

These interpolated results are plotted in Figure 11.
It will be seen that each set of three points form approximately straight lines nearly parallel.

The equations of the simplest curves going through each set of points are:

\[ \text{full intensity} \]
\[
= 10960 - 21.7 \left( \text{HCl} \right) - 0.0474 \left( \text{HCl} \right)^2
\]

\[ \text{reduced intensity} \]
\[
= 11484 - 23.47 \left( \text{HCl} \right) - 0.0354 \left( \text{HCl} \right)^2
\]

Wore the lines completely straight the terms in \((\text{HCl})^2\) would disappear.

Also from Table 25 we may construct an interpolated table to show the variation of quantum efficiency with absorbed intensity under the conditions of experiment at various pressures of HCl. This relationship has customarily been given by the exponent \(n\) in the expression "the rate of HCl formation is proportional to the \(n\)th power of the absorbed intensity", which may also be expressed as \(x I_{\text{abs}}^{1-n} = \text{constant}\).

<table>
<thead>
<tr>
<th>Pressure of HCl (mm.)</th>
<th>I_{\text{abs}}</th>
<th>(\gamma)</th>
<th>Ratios</th>
<th>(1-n)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12.3</td>
<td>10500</td>
<td>3.73</td>
<td>1.05</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>11000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.7</td>
<td>7500</td>
<td>3.0</td>
<td>1.07</td>
<td>0.0616</td>
</tr>
<tr>
<td>125</td>
<td>3.9</td>
<td>3000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.650</td>
<td>3650</td>
<td>3.68</td>
<td>1.20</td>
<td>0.140</td>
</tr>
<tr>
<td>225</td>
<td>3.45</td>
<td>4400</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus the exponent \(n\) decreases with increasing concentration of HCl.
In order to compare the present results with those of other workers, it is desirable here to give a table showing the absolute intensities in quanta per second for the system. The calculations for this are as follows:

\[
\text{Number of quanta} = \frac{\text{Number of HCl molecules formed}}{\text{Quantum Efficiency}}
\]

\[
\text{Quantum Efficiency} = \frac{d \ \text{HCl} \times \text{Avogadro's number} \times \text{Vol. (c.c.)} \times 273}{760 \times 22.4 \times 1000 \times 298}
\]

\[
\text{Number of quanta per second} = \frac{d \ \text{HCl} \times 6.06 \times 10^{23} \times 31.34 \times 273}{t(\text{secs.}) \times 760 \times 22.4 \times 1000 \times 298}
\]

The following table gives the results so calculated for 16 experiments, which cover the whole scope of the results.

### TABLE 28

<table>
<thead>
<tr>
<th>Approx. Cl₂ Pressure</th>
<th>Approx. HCl Pressure</th>
<th>Intensity</th>
<th>No. of Quanta per sec. x (10^{-13})</th>
<th>Serial Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 mm.</td>
<td>15 mm.</td>
<td>Full</td>
<td>9.0</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduced</td>
<td>2.68</td>
<td>30</td>
</tr>
<tr>
<td>28 mm.</td>
<td>16 mm.</td>
<td>Full</td>
<td>7.04</td>
<td>45</td>
</tr>
<tr>
<td>36 mm.</td>
<td>31 mm.</td>
<td>Full</td>
<td>9.72</td>
<td>38</td>
</tr>
<tr>
<td>59 mm.</td>
<td>17 mm.</td>
<td>Full</td>
<td>11.95</td>
<td>46</td>
</tr>
<tr>
<td>45 mm.</td>
<td>125 mm.</td>
<td>Full</td>
<td>8.6</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduced</td>
<td>3.72</td>
<td>57</td>
</tr>
<tr>
<td>45 mm.</td>
<td>125 mm.</td>
<td>Full</td>
<td>10.28</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduced</td>
<td>2.88</td>
<td>64</td>
</tr>
</tbody>
</table>

The table includes the results for various pressures and intensities, providing a comprehensive view of the experimental data.
As stated in the General Introduction, in these experiments the time of reaction was shortened to approximately one tenth as compared with those of Ritchie and Norrish, by increasing the intensity, as it appeared from their conclusions that the value of the exponent of the velocity of HCl formation would thereby tend to the value 0.5. Their observed value was 0.6. Actually the result has been the very reverse. The conditions of experiment of the two researches are very similar apart from the magnitude of intensities. It seems probable therefore that there is no proportional relationship between rate of reaction in the gas phase and a constant power of the absorbed intensity, masked under conditions of experiment by surface action, but that instead of a constant power we may expect to obtain an exponential progressively changing as the intensity is reduced. That in fact a condition of this type does exist has been established in this Department by other workers (M. Ritchie and D. Taylor) since the completion of these experiments. As the intensity increases the index of the quantum efficiency (1 - n) approaches zero. If a mechanism involving Cl₂ molecules is concerned, high concentration of Cl₂ combining with itself will lead to an expression in which the quantum efficiency is independent of the absorbed/
absorbed intensity.

The tendencies which appear to be shown in these results may be summarized as follows:

1. The quantum efficiency rises with increasing chlorine pressure till a maximum is attained at approximately 37 mm. whereafter it steadily declines. This appears to hold with HCl concentrations up to at least 125 mm.

2. The magnitude of the retarding effect of HCl on the quantum efficiency is approximately proportional to the concentration of this gas. If third body recombination alone were responsible for the variation of the quantum efficiency with the concentration of HCl then

\[ \gamma = \frac{a}{\text{Cl}_2 (\text{Cl}_2 + k \text{HCl})} \]

hence \[ \frac{\gamma^{(0)}}{\gamma^{(2)}} = \frac{\text{Cl}_2 + k \text{HCl}_{(2)}}{\text{Cl}_2 + k \text{HCl}_{(1)}} \]

From Figure 11 extrapolating values for HCl = 0 with \( \text{Cl}_2 = \text{H}_2 = 40 \) mm. we get \( \gamma = 11000 \) (full intensity) \( \gamma' = 11500 \) (reduced intensity). From the above formula we can then calculate values for the constant k.

TABLE 39/
TABLE 29

\[ \text{Cl}_2 = \text{H}_2 = 40 \text{ mm.} \]

<table>
<thead>
<tr>
<th>HCl(^{1})</th>
<th>HCl(^{2})</th>
<th>( \gamma^{(1)} )</th>
<th>( \gamma^{(2)} )</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Intensity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>11000</td>
<td>10500</td>
<td>0.095</td>
</tr>
<tr>
<td>0</td>
<td>125</td>
<td>11000</td>
<td>7500</td>
<td>0.15</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>11000</td>
<td>3650</td>
<td>0.356</td>
</tr>
<tr>
<td>Reduced Intensity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>11500</td>
<td>11000</td>
<td>0.091</td>
</tr>
<tr>
<td>0</td>
<td>125</td>
<td>11500</td>
<td>8000</td>
<td>0.14</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>11500</td>
<td>4400</td>
<td>0.287</td>
</tr>
</tbody>
</table>

From Table 29 we see that the value of \( k \) is not constant, as it would be were third body action the only effect of HCl.

There would appear therefore to be some other factor, which is greatest at low pressure of HCl, and falls off as the pressure of that gas rises. If surface action is present the expression will have the form:

\[
\frac{a}{\text{Cl}_2(\text{Cl}_2 + k \text{ HCl}) + S}
\]

where \( S \) is a factor representing surface action. If \( k \) is to be constant then \( S \) must decrease with increase in/
in the pressure of HCl. Thus the results would appear not inconsistent with HCl having two roles, both of which were present in the photo-expansion experiments, namely action as a third body in bringing about the recombination of chlorine atoms in the gas phase, and the prevention of recombination at the surface of the vessel.

3. With increasing concentration of HCl the intensity exponent of the rate of reaction declines. The actual results were:

at 20 mm. HCl \( n = 0.963 \)
at 125 mm. HCl \( n = 0.938 \)
at 225 mm. HCl \( n = 0.860 \).
5. DISCUSSION AND CONCLUSIONS.

The preceding analysis of the experimental results has indicated that, in agreement with the data of Allmand and co-workers, the quantum efficiency of hydrogen chloride formation rises to a maximum and then declines as the pressure of chlorine is increased. This appears to be true even when the concentration of HCl is varied from 15 to 125 mm., although the data are unfortunately insufficient to show whether or not the change in HCl pressure causes the position of the maximum to alter. For the particular reaction vessel employed, the optimum pressure of chlorine is of the order 40 mm.

At low pressures of chlorine, relatively many atoms will reach the walls of the reaction vessel and, by adsorption, will be prevented from participating further in the reaction chains of the gas phase. As the pressure increases, diffusion to the walls will become less and less, and consequently the quantum efficiency will increase. In so far as diffusion alone is the main factor under consideration, increase in pressure of any gas should act in the same way, although the magnitude of the effect will be dependent on the diffusion constants of the particular molecules concerned. At very high pressures of added gas, diffusion/
diffusion to the walls will become inappreciable and then the quantum efficiency should be at a maximum. The previous study of the Budde effect, however, has shown that added gases may have effects other than that connected with diffusion alone; the reaction 
\[ \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_3 + M \]
has been found to be necessary. As the pressure of Cl\(_2\) or other added gas is increased, Cl atoms will be removed by this means in increasing numbers, and if the resulting Cl\(_3\) complexes are removed by mutual recombination, a fall in quantum efficiency is to be expected. The existence of a maximum at an intermediate pressure of chlorine may thus be accounted for. From this point of view, the position of the maximum with reference to the optimum chlorine pressure would in general differ with the pressure of hydrogen chloride which is present; as has been noted, the data at present available are too scanty to enable a decision to be made on this point.

One other factor which must be considered in this connection is the efficiency of removal of Cl atoms at the walls. Allmand and co-workers have shown that the presence of water vapour may decrease the quantum efficiency by reason on an enhanced efficiency of adsorption of chain carriers by a wall carrying adsorbed water-vapour. There is no doubt that a considerable amount of HCl is adsorbed by a silica surface such as is/
is involved in the present experiments, and it has already been noted that a soft glass surface will relatively adsorb much more. In general, one would expect the most easily condensable gases to show the greatest adsorption, and a consequently relatively great change in surface efficiency of adsorption of chlorine atoms; from this point of view the non-appearance of the "abnormal" effect (p. 19) with HCl and CO₂ in the photo-expansion of chlorine is perhaps not surprising. In the present case of the quantum efficiency of HCl formation, it may be deduced that the relative rates of removal of Cl atoms from the gas phase are not necessarily given by the diffusion calculations previously applied, since the surface factors are probably different; at the same time, at high pressures of such gases the proportion of atoms reaching the wall will become very small and this effect will in turn become negligible. Thus there will always arrive a pressure of chlorine at which wall reaction is extremely small, whilst an increasing number of Cl atoms will be removed in the gas phase with a steady decrease in quantum efficiency. Similarly, HCl may accelerate or retard the main reaction, by diffusion and third body effects respectively.

With increasing concentration of HCl the intensity exponent (n) of the rate of reaction decreases, the/
the relative reduction of intensity being kept the same for each pair of results. While from a comparison of the present results with those of Ritchie and Norrish, and of Chapman and Gibbs, we have concluded that it is probable that no fixed value of \( n \) is likely to be found where \( I_{\text{abs}} \) is a complete variable, yet this in no way invalidates the use of the exponent as a measure of variation of quantum efficiency, with a fixed ratio of intensities used throughout, while altering the concentration of HCl. The decrease of the exponent with increase in the pressure of HCl, means that the more HCl there is present the greater is the relative increase of the quantum efficiency when the intensity is reduced by a constant factor.

In the region studied in these experiments the retarding effect of HCl is approximately proportional to the concentration of that gas. In our consideration of the possible reactions of HCl we were able to find only two which appeared at all probable.

1. Action as a third body.
   \[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 \text{M} \]

2. Removal of hydrogen atoms.
   \[ \text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl} \]

In addition however, the extent of its presence modifies the values of the constants for the wall reactions of Cl and Cl\(_3\). We are faced here with the difficulty/
difficulty that the line relating quantum efficiency and HCl pressure is only approximately straight, and may be the sum of more than one tendency none of which may obey a straight line law.

It was concluded earlier that there are 6 well established reactions which almost undoubtedly take place.

1. \( \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl} \)
2. \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)
3. \( \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \)
4. \( \text{Cl} + \text{Cl}_2 + M \rightarrow \text{Cl}_3 + M \)
5. \( 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \)
6. \( \text{Cl} \rightarrow \frac{1}{2} \text{Cl}_2 \) at surface

Consider what kinetic expression these reactions alone would give rise to;

\[
\begin{align*}
\frac{d}{dt} \text{HCl} & = k_2 [\text{Cl}] [\text{H}_2] + k_3 [\text{H}] [\text{Cl}_2] = 2k_3 [\text{H}] [\text{Cl}_2] \\
\frac{d}{dt} \text{H} & = k_2 [\text{Cl}] [\text{H}_2] - k_3 [\text{H}] [\text{Cl}_2] = 0 \\
\frac{d}{dt} \text{Cl} & = k_1 \text{I}_{\text{abs}} - k_2 [\text{Cl}] [\text{H}_2] + k_3 [\text{H}] [\text{Cl}_2] - k_M [\text{Cl}] [\text{Cl}_2][M] - s [\text{Cl}] = 0 \\
[\text{Cl}] & = \frac{k_1 \text{I}_{\text{abs}}}{(k_M [\text{Cl}_2][M] + s)} \\
\frac{d}{dt} \text{HCl} & = 2k_2 [\text{H}_2] [\text{Cl}] = 2k_2 [\text{H}_2] k_1 \text{I}_{\text{abs}} / (k_M [\text{Cl}_2][M] + s) \\
\gamma & = \frac{2k_1 k_2 [\text{H}_2]}{(k_M [\text{Cl}_2][M] + s)}
\end{align*}
\]

This expression has the following features:-

1. The quantum efficiency is proportional to the concentration of hydrogen. This is a generally accepted requirement.
2. The concentration of chlorine term, appearing in/
in the divisor, would give rise to a steady fall in the quantum efficiency with increased chlorine pressure.

3. The concentration of third body \( M \) term, in the divisor, would give a retarding effect for HCl, which might under certain conditions approximate to a nearly linear condition over a limited region.

4. As the expression stands there is nothing to allow of change of quantum efficiency with intensity.

Consider now how the expression is varied if we admit other reactions to our scheme. In our previous consideration we suggested three others as possible. These were:

7. \( \text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl} \) 
   \( k_7 \)

8. \( \text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl} \) 
   \( k_8 \)

9. \( \text{Cl} \rightarrow \text{destruction at the wall} \) 

If we add reaction 8 to our mechanism, then

\[
\frac{d[\text{Cl}]}{dt} = k_1 I_{\text{abs}} - k_2 [\text{Cl}][\text{H}_2] + k_3 [\text{Cl}_2][\text{H}] - k_M [\text{Cl}][\text{Cl}_2][M] - S[\text{Cl}] + k_8 [\text{H}][\text{HCl}] = 0.
\]

\[
\frac{d[\text{H}]}{dt} = k_2 [\text{H}_2][\text{Cl}] - k_3 [\text{H}][\text{Cl}_2] - k_8 [\text{H}][\text{HCl}] = 0.
\]

from which we obtain the relation:

\[
\gamma = \frac{2 k_1 k_2 k_3 [\text{H}_2][\text{Cl}_2]}{(k_3 [\text{Cl}_2] + k_8 [\text{HCl}]) (k_M [\text{Cl}_2][M] + S)}
\]

This varies from the previous equation by containing the factor

\[
\frac{k_3 [\text{Cl}_2]}{k_3 [\text{Cl}_2] + k_8 [\text{HCl}]}
\]
To a limited extent this factor might sometimes cause an optimum value for the quantum efficiency with increasing chlorine. But this tendency can be accounted for by the variations of $S$, and it is agreed by nearly all workers that the extent of reaction 8 is small. This factor will accordingly approximate to unity throughout, unless the concentration of HCl is very large. We cannot hope by this method to get much information of the extent of the reaction, and can only fall back on the conclusions of other workers that it takes place to a limited extent only.

Reaction 9. $\text{Cl}_3 \rightarrow$ destruction at surface is unlikely to give rise to any chlorine atoms which are not almost immediately adsorbed on the walls, and do not enter the main body of the gas phase. So long as this is the case the above kinetic expression will in no way be altered.

We have now to consider reaction 7

$$\text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl}$$

which may occur with or without the assistance of a third body. If any chlorine atoms should have entered the gas phase as a result of reaction 9 such an occurrence may be considered as only a special case of reaction 7. For reactions 1 - 7 we obtain by the usual methods the kinetic expression

$$\gamma = \frac{2 k_2 k_3 [H_2]}{k_M [\text{Cl}_2][M] + S} + \frac{2 k_2 k_7 [H_2][\text{Cl}_3]}{(k_M [\text{Cl}_2][M] + S) I_{abs}}$$
where
\[ [\text{Cl}_3] = \frac{-k_7 S + \sqrt{(k_7 S)^2 + 4(k_M[\text{Cl}_2][M]k_5 + k_5 S)k_1 I_{abs} k_M[\text{Cl}_2][M]}}{2(k_M[\text{Cl}_2][M]k_5 + k_5 S)} \]

At high pressure of HCl, S tends to zero, as relatively few chlorine atoms will now reach the walls. Put S = 0.

\[ \gamma = \frac{2 k_2 k_1[H_2]}{k_M[\text{Cl}_2][M]} + \frac{2 k_2 k_7[H_2]}{k_M[\text{Cl}_2][M]I_{abs}/k_1} \]

Thus at high HCl we have the quantum efficiency equal to the sum of two terms, in the first of which the rate exponent \( n \) is unity, and in the second tends to 0.5. This agrees with the tendency of the quantum efficiency to become independent of \( I_{abs} \) at high intensity, while at low intensity it tends to become proportional to \( 1/\sqrt{I_{abs}} \). It will be seen from the expression that, neglecting surface action, Cl\(_2\) not merely retards the reaction, but under certain conditions will do so proportionally to the square of its concentration, since if \([\text{Cl}_2]\) is large compared with \([\text{HCl}]\) then \( k_M[\text{Cl}_2][M] \approx k_M[\text{Cl}_2]^2 \).

We may modify the above expression to allow the decomposition of Cl\(_3\) in the gas phase to occur after collision with another molecule \( M \). This alters \( k_7 \) to \( k_7[M] \) but otherwise makes no change.

Then
\[ \gamma = \frac{2 k_2 k_1[H_2]}{k_M[\text{Cl}_2][M] + S} + \frac{2 k_2 k_7[M][H_2][\text{Cl}_3]}{k_M[\text{Cl}_2][M] + S} \]
where
\[
[\text{Cl}_3] = \frac{-k_7 S[M] + \sqrt{(k_7 S[M])^2 + 4(k_M[\text{Cl}_2][M]k_5 + k_5 S_k I_{abs}k_M[\text{Cl}_2][M])}}{2(k_M[\text{Cl}_2][M] + k_5 S)}
\]

Where the concentrations of gases are sufficiently great to make surface action negligible the approximation becomes
\[
\gamma = \frac{2 k_2 k_1 [H_2]}{k_M[\text{Cl}_2][M]} + \frac{2 k_2 k_7 [H_2]}{k_M[\text{Cl}_2] \sqrt{k_5 I_{abs}/k_1}}
\]

If the intensity is very great the first term will be the most important and the quantum efficiency will become nearly independent of \(I_{abs}\). On the other hand if the pressure of HCl or an inert gas is very great while the intensity is relatively small we may omit the first term and
\[
\gamma = \frac{2 k_2 k_7 [H_2]}{k_M[\text{Cl}_2] k_5 I_{abs}/k_1}
\]

Hence at high pressure of HCl the reaction ceases to be further retarded by it. This is perhaps one of the reasons why this retardation was not observed by many workers.

Since we are dealing here with very high values of \(I_{abs}\) it is possible that the reaction
\[
\text{Cl} + \text{Cl}_3 \rightarrow 2\text{Cl}_2
\]
should also be considered. This leads to a very complicated calculation, and there is no/
no advantage in discussing it further without fuller data.

The following summary may be made of the above conclusions. The results obtained are not inconsistent with the mechanism:

1. \( \text{Cl}_2 \xrightleftharpoons[\text{hv}]{\text{Cl} + \text{Cl}} \)
2. \( \text{Cl} + \text{H}_2 \xrightarrow{\text{HCl} + \text{H}} \)
3. \( \text{H} + \text{Cl}_2 \xrightarrow{\text{HCl} + \text{Cl}} \)
4. \( \text{Cl} + \text{Cl}_2 + \text{M} \xrightarrow{\text{Cl}_3 + \text{M}} \)  
5. \( 2 \text{Cl}_3 \xrightarrow{} 3 \text{Cl}_2 \)
6. \( \text{Cl} \xrightarrow{\frac{1}{2} \text{Cl}_2} \) at surface
7. \( \text{Cl}_3 \xrightarrow{(\text{M})} \text{Cl}_2 + \text{Cl} \)  

with the probable additional reactions

8. \( \text{H} + \text{HCl} \xrightarrow{} \text{H}_2 + \text{Cl} \)
9. \( \text{Cl}_3 \xrightarrow{} \) destruction at surface

This on analysis appears to exhibit all the tendencies which the present results in conjunction with those of certain other workers require.

Reactions 1 - 7 give the expression

\[
\gamma = \frac{2 k_2 k_1 [\text{H}_2]}{k_M [\text{Cl}_2][\text{M}] + S} + \frac{2 k_2 k_7 [\text{M}][\text{H}_2][\text{Cl}_3]}{k_M [\text{Cl}_2][\text{M}] + S}
\]

where

\[
[\text{Cl}_3] = \frac{-k_7 S [\text{M}]}{2(k_M [\text{Cl}_2][\text{M}] + k_5 S)} + \sqrt{\frac{k_7 S [\text{M}]}{2(k_M [\text{Cl}_2][\text{M}] + k_5 S)} + \frac{4(k_M [\text{Cl}_2][\text{M}] k_5 + k_5 S)k_{1 abs} k_M [\text{Cl}_2][\text{M}]}{2(k_M [\text{Cl}_2][\text{M}] + k_5 S)}}
\]

1. The quantum efficiency is proportional to the concentration/
concentration of hydrogen.

2. The divisor term \((k_M [Cl_2] [M] + S)\) would cause the quantum efficiency to increase initially with the concentration of chlorine, due to the decline of surface action represented by the factor \(S\). As surface action becomes relatively unimportant the steady growth of \(k_M [Cl_2] [M]\) causes the quantum efficiency to pass through a maximum and then decline. The observed retarding effect of HCl is also not inconsistent with this divisor.

3. Where the concentrations of gases are sufficient to render surface action negligible the quantum efficiency would be given by

\[
\gamma = \frac{2 k_2 k_1 [H_2]}{k_M [Cl_2] [M]} + \frac{2 k_2 k_7 [H_2]}{k_M [Cl_2] \sqrt{k_5 I_{abs}/k_1}}
\]

which can be tested by two limiting cases.

4. In 3 as the intensity increases the second term declined and the quantum efficiency tends to become independent of the intensity. This is in accordance with comparison of these results with those of Ritchie and Norrish, which shows that the exponent for the rate of HCl formation tends to increase with increasing intensity.

5. Where the pressure of HCl or an inert gas is very great, the first term declines, and the quantum efficiency tends to

\[
\gamma = \frac{2 k_2 k_7 [H_2]}{k_M [Cl_2] \sqrt{k_5 I_{abs}/k_1}}
\]
Thus as the pressure of HCl increases the quantum efficiency should become proportional to $1/I_{abs}^{\frac{1}{n}}$ which is consistent with the present results. The retarding effect of HCl should tend to disappear at high pressure of this gas.

In conclusion, attention may be directed to an alternative process to which some of the experimental trends above noted may be partly due. The combination of hydrogen and chlorine is attended by the production of a considerable quantity of heat, as expressed by the equation $H_2 + Cl_2 \rightarrow 2HCl + 44000$ cals. Thus, if the rate of reaction be large, as it is in these photo-experiments, convection may be a factor of importance. It is, for example, possible that an increased $I_{abs}$ will cause considerably increased convection by reason of the greater heat evolution, and such increased convection would decrease the measured quantum efficiency by increasing the surface removal of chain carriers. In the limit, where all chain carriers were so removed, the rate would be directly proportional to $I_{abs}$; in other words the higher $I_{abs}$, the higher the index $n$, as experimentally indicated. Evidence for such a mechanism has been given for the reaction between illuminated bromine and acetylene (67). Such convection effects will in general be at a minimum at low pressures; if at higher pressures of chlorine convection increases until surface action is predominant a smaller overall quantum efficiency might result.
result, as is also experimentally found.

There is, however, reason to believe that such convection effects should be approximately independent of the nature of the added gas, at least in the cases of $A$, $N_2$, and $HCl$. In the bromine-acetylene reaction referred to above, the increase in rate was more or less independent of the nature of the added gas; further, while the thermal conductivity of a gas, by kinetic theory, is independent of the pressure of such a gas where pressures are not too small in comparison with the size of the containing vessel, the actual measurements of relative thermal conductivities, as described in Part II, showed discrepancies, attributed to convection increasing with increasing pressure but the same for similar pressures of the gases $A$, $N_2$, and $HCl$. The rates of diffusion of $Cl$ atoms through these gases are approximately the same for corresponding pressures; as far as the Budde effect measurements are concerned, therefore, the differences observed between the effects for different gases, cannot be explained by convection alone. Further, in the photosynthesis experiments, the retardation by $HCl$ might be due to convection effects and surface factors, but in this case there is then no reason why the index $\bar{q}$ should decrease as $HCl$ is added. While, therefore, the possibility of convection effects is to be admitted.
admitted, it seems that the experimental results above cannot be explained solely on such a basis. The conclusions drawn regarding the mechanisms of Budde effect and hydrogen chloride photosynthesis are thus regarded as essentially correct, and it is hoped that they may prove a useful ground-work for further investigation.
GENERAL SUMMARY OF THE RESEARCH
The mechanism of the recombination of chlorine atoms in the gas phase has been examined by the measurement of the photo-expansion in the presence of varied concentration of added gases. The results so obtained are in accordance with the reactions:

\[ \text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M} \]

\[ 2\text{Cl}_3 \rightarrow 3\text{Cl}_2 \]

and are not consistent with any other mechanism.

In the course of these observations a new effect has been observed, which is ascribed to the adsorption of \( \text{Cl}_3 \) molecules on the surface of the vessel. When the vessel was illuminated, the pressure, after increasing to a maximum, declined to a slightly lower steady value; while on extinction of the light the pressure fell slightly below the original dark pressure of the gas, to which it then returned.

This effect is at a minimum when the pressure of added gas is zero, and chlorine atoms will most readily reach the surface; and again at high pressure of added gas (600 mm.) when diffusion to the wall of any relatively unstable species such as \( \text{Cl}_3 \) is most unlikely. It is at a maximum at an intermediate pressure where there exists a balance between formation of the \( \text{Cl}_3 \) complex, diffusion to the surface, and its removal by mutual recombination.

The/
The absence of this effect in the presence of the "condensable" gases HCl and CO₂ is ascribed to modification of the nature of the wall by an adsorbed layer of these gases. This is in agreement with an abnormality noticeable in the values of the triple collision coefficients, obtained, from the data for the various added gases. Whilst the ratios of the values for O₂ and A with respect to N₂, and for CO₂ to HCl, are in agreement with results of other workers, it is probable that direct comparison cannot strictly be made between the values for the "permanent" and the "condensable" gases.

The effect of water vapour is slight, though small traces appear to lower the Budde effect a little.

Relative measurements of the thermal conductivity of HCl, and of the gas mixtures used in studying the photo-expansion of chlorine, have been made by the hot wire method. The thermal conductivity of HCl was found to be 1.61. For gas mixtures within certain limits, it was found that the conductivity can be calculated with sufficient accuracy on the assumption that conductivity is a linear function of composition i.e. by the formula:

\[ K = (K_M - K_{HCl}) \frac{[M]}{([HCl] + [M])} + K_{HCl} \]

The hydrogen-chlorine reaction has been studied in oxygen-free mixtures, with variation within certain
certain limits of the factors the intensity of the light, the concentration of chlorine, and of the product HCl. The following tendencies were observed for the conditions of experiment:
1. The quantum efficiency of HCl formation rose with increased chlorine concentration till about 37 mm. and thereafter declined.
2. At Cl₂ = H₂ = 40 mm. HCl retarded the rate of reaction. The retarding effect was approximately proportional to the concentration of that gas.
3. With increased concentration of HCl the exponent n decreased, in the expression $\frac{d \text{HCl}}{dt} \propto \frac{n}{\text{abs}}$.

From consideration of possible reactions and the kinetic expressions derived therefrom, it has been found possible to formulate a mechanism consistent with these results. The initial dissociation, the Nernst chain, and the recombination process derived from the photo-expansion results, require the following equations.

1. Cl₂ + hν → Cl + Cl
2. Cl + H₂ → HCl + H
3. H + Cl₂ → HCl + Cl
4. Cl + Cl₂ + M → Cl₅ + M
5. 2Cl₃ → 3Cl₂
6. Cl → $\frac{1}{2}$Cl₂ at surface

The following reactions are held to take place from consideration/
consideration of the present results in conjunction with examination of those of other workers and of theoretical considerations.

7. $\text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl}$

8. $\text{HCl} + \text{H} \rightarrow \text{Cl} + \text{H}_2$

9. $\text{Cl}_3 \rightarrow$ destruction at surface

Reaction 8 is known to occur in an isolated system, though with small probability for any particular collision. It will occur to a very limited extent in this system. It introduces into any kinetic expression a factor which will usually not vary much from unity.

The combination of the destruction of chlorine atoms at the wall:

6. $\text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2$ at surface,

and of the triple collision

4. $\text{Cl} + \text{Cl}_2 + \text{M} \rightarrow \text{Cl}_3 + \text{M}$

leads to an expression for the quantum efficiency in which the denominator is $(k_	ext{M} [\text{Cl}_2] [\text{M}] + S)$. At low pressure of chlorine the first term is small, and this factor approximates to $S$, which is large as a high proportion of atoms reach the walls. As chlorine increases fewer atoms will diffuse to the surface and $S$ decreases causing the quantum efficiency to rise to a maximum from which it declines due to growth of the term $k_4 [\text{Cl}_2] [\text{M}]$.

In conjunction with equations 1 - 6 the reaction:

7. $\text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl}$

gives the expression/
\[ \gamma = \frac{2k_1 k_2 [H_2]}{k_M [Cl_2][M] + S} + \frac{2k_2 k_7 [M][H_2][Cl_3]}{(k_M [Cl_2][M] + S)I_{abs}} \]

where

\[ [Cl_3] = \frac{-k_6 k_7 [M] + \sqrt{(k_6 k_7 [M])^2 + (k_M [Cl_2][M] k_5 + k_6 k_5 4k_1 I_{abs} k_M [Cl_2][M])}}{2(k_M [Cl_2][M] k_5 + k_6 k_5)} \]

Where the concentration of gases is sufficient to permit surface action to be neglected, this approximates to

\[ \gamma = \frac{2k_2 k_1 [H_2]}{k_M [Cl_2][M]} + \frac{2k_2 k_7 [H_2]}{k_M [Cl_2][M]^{1/2} I_{abs}} \]

Where in addition the intensity is high, the quantum efficiency should tend to become independent of the intensity, which is in accordance with a comparison of the present results with those of Ritchie and Norrish. On the other hand, as the pressure of HCl increases the second term becomes more important than the first, and the exponent in the equation \( I_{abs} \gamma = \text{constant} \) should tend to 0.5. Such a tendency has been observed.

I wish to express my gratitude to my supervisor, Dr Ritchie, for the great encouragement and assistance he has given me throughout the course of the work. I also thank Professor Kendall for providing facilities for this research, and the Trustees of the Moray Research Fund for grants for apparatus.
TABLE OF REFERENCES.

   Ibid 140 112 (1933)
   Ibid 140 713 (1933)

2. E. Budde Phil. Mag. (4) 42 290 (1871)
   Wied. Ann. 144 313 (1871)
   J. prakt. Chem. 7 376 (1873)
   Pogg. Ann. Ergbd. 6 477 (1873)

3. A. Richardson Phil. Mag. (5) 32 277 (1891)

4. H.B. Baker B.A. Reports, 493 (1894)


8. J.W. Mellar J. Chem. Soc. 81 1289 (1902)


    Ibid 31 983 (1928)


12. W. Nernst Zeit. Elektrochemie 24 355 (1918)

13. R. Gehringer Zeit. Elektrochemie 27 511 (1921)

14. N. Thom Fortschritte der Chemie, 18 Heft 11 (1926)


Ibid 1878 (1937)
G.E. Gibson and N.S. Bayliss Phys. Review 44 188 (1933)
see also A. Farkas and H.W. Melville "Experimental Methods in Gas Reactions" page 210.
38. E. Moles Comptes Rendues 205 1391 (1937)
40. A. Farkas and H.W. Melville "Experimental Methods in Gas Reactions" page 283
41. H. Senftleben and O. Reichmar Ann. Physik. 6 112 (1930)
42. Cruickshank Nicholson's Journal 5 202 (1801)
43. J.W. Draper Phil. Mag. 19 195 (1841)
        Ibid 23 401 (1843)
        Ibid 27 327 (1845)
        Phil. Mag. 146 355 (1857)
        Ibid 146 601 (1859)
        Ibid 148 879 (1859)
        Ostwald's Klassiker 34, 38 (Leipzig 1892)
45. A. Goehn and G. Jung Zeit. phys. Chem. 110 705 (1924)
47. Seebeck Goethe's Farbenlehre (1810)
49. W. Taylor, Phil. Mag. 49 1165 (1925)
50. F. Weigert, Z. phys. Chem. 120 215 (1926)
      Allmand
52. N.S. Bayliss, Trans. Faraday Soc. 33 1339
      (1937)
      R.G. Aickin and N.S. Bayliss, Ibid 33 135
      (1937)
      Ibid 24 355 (1918)
      375 (1931)
55. K.H. Geib and P. Harteck, Zeit. phys. Chem. 15 B
      116 (1931)
56. C.H. Burgess and D.L. J. Chem. Soc. 89 1399 (1906)
      Chapman
      Ibid 97 845 (1909)
      D.L. Chapman, Trans. Faraday Soc. 21 547
      (1925)
      (1913)
58. M. Bodenstein and W. Unger, Zeit. phys. Chem. 11 B 253
      (1930)
60. J.A. Christiansen, Zeit. phys. Chem. 2 B 413 (1929)
      (1937)
62. J.C. Potts and G.K. Rollefson, J. Amer. Chem. Soc. 57 1027
      (1935)
      Klasse 1 (1936).
64. G.M. Schwab  
Zeit. phys. Chem. 173 123 (1936)

65. G.E. Kimball and H. Eyring  
J. Amer. Chem. Soc. 54 3876 (1932)

66. G.K. Rollefson  
J. Amer. Chem. Soc. 56 579 (1934)

67. K.L. Müller and H.J. Schumacher  