THE KINETICS AND SPECTROSCOPY OF THE RECOMBINATION
OF CHLORINE ATOMS IN A LOW PRESSURE FLOW SYSTEM

by

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We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1964
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The University of British Columbia, Vancouver 8, Canada

Date May 7, 1964.
ABSTRACT

The kinetics of the recombination of chlorine atoms has been studied in a fast flow system in the pressure range 0.2 to 2.0 mm Hg. The gas phase recombination was found to follow the reaction

\[ \text{Cl} + \text{Cl} + M \rightarrow \text{Cl}_2 + M \quad (1) \]

with

\[ - \frac{d[\text{Cl}]}{dt} = 2k_{1M}[\text{Cl}]^2[M] \quad (1a) \]

Rate constants were determined for He and Cl\textsubscript{2} as third bodies in the reaction where

\[ k_{1\text{Cl}_2} = 2.45 \times 10^{16} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \]

and

\[ k_{1\text{He}} = 0.5 \times 10^{16} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \]

Concurrent with this reaction was a surface recombination which may be written

\[ \text{Cl} + \text{wall} \rightarrow \frac{1}{2}\text{Cl}_2 + \text{wall} \quad (26) \]

having a surface recombination coefficient \( \gamma = 6.81 \times 10^{-5} \), calculated from \( k_{2\text{g}} = 3.9 \text{ sec}^{-1} \). No low pressure change in the kinetic order could be detected under the experimental conditions used.

The emission accompanying the recombination was found to be a band spectrum of a \( 3\Pi_{0u} \rightarrow 1\Sigma_g^+ \) transition.
The emission decayed according to the relation

\[ I = \frac{-\text{d}h\Psi}{\text{d}t} = k_{41} [\text{Cl}]^2 [\text{M}] \quad (41) \]

indicating that the \( ^3\gamma \text{Ou}^+ \) state is formed in some atom recombination process.
ACKNOWLEDGEMENTS

The author wishes to express his most sincere thanks to Dr. E. A. Ogryzlo for his enthusiastic guidance of this research and for the many enlightening discussions with the author during the course of the project.

The author also wishes to thank Dr. A. V. Bree for his assistance with the spectroscopic aspects of the research.
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\]
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\]
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\[ \bigcirc \] Band Spectra
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INTRODUCTION

The homogeneous, gas phase recombination of atoms is known to be a termolecular reaction which may be written

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

Here A represents the atomic species and M, a third body or "chaperon" \(^1\) which, in some manner, removes the energy of the A-A bond formation and stabilizes the newly formed A\(_2\) molecule. The rate constant, \(k_M\), is so written to indicate its dependence on the identity of M in the reaction.

Despite the apparent simplicity of the reaction it is only in recent years, with new experimental techniques (microwave, shock tube, flash photolysis), that some of the rate constants and activation energies have been determined to any degree of accuracy. Though rate constants for the recombination of H, O, N, I and Br atoms have been determined \(^2\) with various third body gases, no kinetic mechanism has been proposed which is universally accepted by all workers in the field. Moreover, studies of Cl atom recombination have been singularly unsuccessful and no accurate determinations of the rate constant or activation energy have been reported.

a) Chlorine Atom Recombination

The recombination of chlorine atoms, which may be written
Cl + Cl + M \rightarrow Cl_2 + M \quad (1)

occurs in many systems. Lack of knowledge of the rate constant or mechanism has forced investigators either to assume an order of magnitude rate constant by analogy with known recombinations or to work under conditions where the recombination is negligible with respect to other reactions.

Despite the many new experimental methods available, few investigations have been conducted which are specifically intended to study the chlorine atom recombination reaction.

A few workers have approached the subject with varying degrees of success. Rodebush and Klingelhoefer and Schwab and Friess in 1933 independently reported the production of chlorine atoms with an electrical discharge in a flow system. In a more detailed paper in 1934 Schwab reported that the fast recombination of the atoms on the quartz or glass surface of the reaction system precluded any study of the gas phase recombination.

This conclusion apparently discouraged much further investigation of the subject. Trotman-Dickenson in 1955 stated "Despite numerous attempts, no accurate values of the rate constants for the combination of hydrogen, oxygen
and chlorine atoms have yet been determined".

A great number of workers have studied systems in which chlorine atom recombination occurs, particularly as a chain termination step. These include Porter and Wright 7 who studied Cl₂ + O₂ mixtures by flash photolysis, Knox 8, and Dainton and co-workers 9 who studied the photochlorination of hydrocarbons. They all recognize that reaction (1) is one chain termination step in their kinetic schemes but attempted to work under conditions where atom recombination is negligible with respect to other reactions, e.g. radical-radical combinations. In only one paper in the series by Dainton et al do they give a numerical value for k₁Cl₂

\[ k_{Cl_2} = 6.5 \times 10^{17} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \text{ at } 40^\circ \text{C} \text{ and } 7.2 \times 10^{17} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \text{ at } 62^\circ \text{C} \].

Hiracka and Hardwick 10 have reported determination of the rate constant at 1600\(^0\)K in a shock tube. They gave a value of \(2.5 \times 10^{15} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}\) at this temperature and derive an equation from which a value of \(3.3 \times 10^{16} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}\) at 40\(^0\)C can be calculated, though the accuracy of such an extrapolation is doubtful.

Another determination has been alluded to by Martens 11 in a Faraday Society discussion. He quotes an approximate value of \(2 \times 10^{16} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}\) but gives no further
particulars. He is no doubt referring to work published by Martens, Goldfinger et al.\textsuperscript{12} on the chlorination of CO carried out at about 600°K. Their results give \( k_{1Cl_2} = 4 \times 10^{15} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \) and report a negative activation energy of about 1 kcal mole\(^{-1}\) at 600°K.

b) Bromine and Iodine Atom Recombination

In contrast to the dearth of material on chlorine atom recombination there is a great deal in the literature on bromine and iodine atom recombination. The reason for this specialization is, no doubt, the ease of study of these systems where the large values of the extinction coefficients permit high atom concentrations by photolysis. This same factor also permits more accurate photometric measurement of their concentrations in the reaction systems of flash photolysis or shock tubes. The theoretical discussions on the subject have, of necessity, confined themselves to bromine and iodine in order to test their proposals.

Table I presents a brief summary of the results of flash photolysis studies on the recombination of iodine atoms by Porter and Smith\textsuperscript{13}. This data is perhaps the most representative available to date. Table I also gives some results on bromine atom recombination. Bromine has
Table I

Iodine Atom Recombination

<table>
<thead>
<tr>
<th>Third body</th>
<th>( k \times 10^{-16} ) cm(^6) moles(^{-2}) sec(^{-1} )</th>
<th>(-\Delta E) kcal/mole</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>0.15</td>
<td>0.4</td>
<td>13</td>
</tr>
<tr>
<td>Argon</td>
<td>0.30</td>
<td>1.3</td>
<td>13</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.67</td>
<td>1.5</td>
<td>13</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>1.34</td>
<td>1.75</td>
<td>13</td>
</tr>
<tr>
<td>Benzene</td>
<td>7.95</td>
<td>1.7</td>
<td>13</td>
</tr>
<tr>
<td>Toluene</td>
<td>19.3</td>
<td>2.7</td>
<td>13</td>
</tr>
<tr>
<td>Ethyl Iodide</td>
<td>26.0</td>
<td>2.4</td>
<td>13</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>40.2</td>
<td>4.1</td>
<td>13</td>
</tr>
<tr>
<td>Iodine</td>
<td>138.0</td>
<td>-</td>
<td>13</td>
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</table>

Bromine Atom Recombination

<table>
<thead>
<tr>
<th></th>
<th>( k \times 10^{-16} ) cm(^6) moles(^{-2}) sec(^{-1} )</th>
<th>(-\Delta E) kcal/mole</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.10</td>
<td>0.47</td>
<td>14</td>
</tr>
<tr>
<td>Argon</td>
<td>0.19</td>
<td>1.40</td>
<td>15</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.17</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.39</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.40</td>
<td>1.20</td>
<td>15</td>
</tr>
<tr>
<td>Bromine</td>
<td>13.0</td>
<td>1.38</td>
<td>14</td>
</tr>
</tbody>
</table>

\((\Delta E \text{ from } k = A \exp(-\Delta E/RT))\)
not been studied quite as extensively as has iodine, most investigations having been conducted with shock tubes at high temperatures.

The similarities in rate constants and activation energies in the two recombination systems is easily seen.

c) Mechanisms

Any mechanism proposed for the recombination reaction must explain a number of facts which are readily observed in table I:

i) There is a large variation in the efficiencies of various chaperons.

ii) There is a negative temperature coefficient usually reported as a "negative activation energy".

iii) There is some relationship between the chaperon efficiency and the magnitude of the negative activation energy.

If we assume that the observed third order kinetics result from a termolecular process, two distinct reaction paths are conceivable. The first of these requires an energetic Cl$_2^*$ molecule initially, which is deactivated by collision with M.
A) \[ \text{Cl} + \text{Cl} \rightleftharpoons \text{Cl}_2^* \] \hspace{1cm} (2, 3)

\[ \text{Cl}_2^* + \text{M} \rightarrow \text{Cl}_2 + \text{M} \] \hspace{1cm} (4)

\[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \] \hspace{1cm} (1)

so \[ -\frac{d[\text{Cl}]}{dt} = 2k_2[\text{Cl}]^2 - k_3[\text{Cl}_2^*] \]

Assuming steady state conditions for \([\text{Cl}_2^*]\) this becomes;

\[ -\frac{d[\text{Cl}]}{dt} = \frac{2k_2k_4[\text{Cl}]^2[\text{M}]}{k_3 + k_4[\text{M}]} \]

The rate of reaction (3), the unimolecular decomposition of an excited molecule, is equal to the reciprocal of the lifetime \(\tau\) of \(\text{Cl}_2^*\). It is usually assumed that \(\tau\) is of the order of \(10^{-15}\) sec (one vibrational period of \(\text{Cl}_2^*\)) thus \(k_3 = \frac{1}{\tau} = 10^{13}\) sec\(^{-1}\). Assuming zero activation energy for reaction (4) its rate is dependent on the bimolecular collision frequency. At 0.5 at., \(k_4[\text{M}] = 10^8\) sec\(^{-1}\), thus \(k_3 \gg k_4[\text{M}]\) and equation (5) becomes:

\[ -\frac{d[\text{Cl}]}{dt} = \frac{2k_2k_4}{k_3}[\text{Cl}]^2[\text{M}] \] \hspace{1cm} (6)

which gives the experimentally observed orders with respect to both \([\text{Cl}]\) and \([\text{M}]\). This mechanism, however, fails to account for the negative activation energies since \(k_3\), the rate of unimolecular decomposition of an excited species, has zero activation energy. Moreover it is
incapable of explaining the observed \([M]\) dependence of the reaction since the pre-exponentials of the various rate constants involve only the collisional cross section of the third body, and in general, agreement is poor.

The second simple mechanism involves a \(ClM^*\) intermediate.

\[
B) \quad Cl + M \rightleftharpoons ClM^* \quad (7, 8)
\]
\[
ClM^* + Cl \rightarrow Cl_2 + M \quad (9)
\]
\[
Cl + Cl + M \rightarrow Cl_2 + M \quad (1)
\]

Then \[\frac{-d[Cl]}{dt} = k_7 [Cl] [M] - k_8 [ClM^*] + k_9 [ClM^*][Cl] \quad (10)\]

Steady state assumptions on \([ClM^*]\), and calculations similar to those of mechanism A, in this case requiring \(k_8 \gg k_9 [Cl]\) give

\[\frac{-d[Cl]}{dt} = \frac{k_7 k_9 [Cl]^2 [M]}{k_8} \quad (11)\]

The observed order is again realized.

Since \(M\) is involved in the intermediate complex its chemical behaviour, rather than simply its cross section might be expected to play a more important role. The negative temperature dependence of the rate constant could be attributed to the stability of this complex. Not
explicit in these statements, however, is the fact that this requires a Cl-M bond be formed in the ClM* complex, which however is isoenergetic with the separate species by definition.

Norrish \(^{16}\) maintains that reaction (7) could be a "sticky" collision in which the energy of formation of the bond is momentarily distributed among the increased number of degrees of freedom in the ClM* complex. This theory however fails to completely explain the different efficiencies of the noble gases and does not explain the great efficiency of I\(_2\) noted in iodine atom recombination.

Davidson \(^{17}\) has proposed a more complex mechanism, actually an extension of mechanism B, which holds more promise in being able to explain the observed facts.

\[
\begin{align*}
\text{C)} & \quad \text{Cl} + \text{M} & \rightleftharpoons \text{ClM}^* & \quad (7, 8) \\
& \text{ClM}^* + \text{M} & \rightleftharpoons \text{ClM} + \text{M} & \quad (12, 13) \\
& \text{ClM} + \text{Cl} & \rightarrow \text{Cl}_2 + \text{M} & \quad (14) \\
& \text{Cl} + \text{Cl} + 2\text{M} & \rightarrow \text{Cl}_2 + 2\text{M} & \quad (1 \text{ a})
\end{align*}
\]

This mechanism does not assume an abnormal lifetime for ClM*. It assumes that a bound species ClM can be formed by collision with M in reaction (12).
Analyses of mechanism C shows

\[-\frac{d[Cl]}{dt} = k_7 [Cl] [M] - k_8 [ClM^*] - k_{14} [ClM][Cl]\]

(15)

Assuming steady state concentrations of ClM* and ClM we find

\[-\frac{d[Cl]}{dt} = k_7 [Cl] [M] \left( 1 - \frac{k_8}{k_8 + k_{12}[M]} + \frac{k_{12}k_{14}[Cl][M]}{(k_{13}[M] + k_{14}Cl)[(k_8 + k_{12}[M])]^2} \right)\]

(16)

If \(k_8 \gg k_{12}[M]\) and \(k_{13}[M] \gg k_{14}[Cl]\) then

\[-\frac{d[Cl]}{dt} = \frac{k_7 k_{12} k_{14}}{k_8 k_{13}} [Cl]^2 [M]\]

(17)

once again obtaining the observed kinetic order.

Comparing equation (17) with equation (11) we see that \(k_7 k_{14}\) is identical to \(k_7 k_8\). The proposed advantage of mechanism C obviously lies in the term \(k_{12}/k_{13}\), the equilibrium constant of reaction (12, 13).

If we write the right hand side of equation (15) expression the rate constants in the Arrhenius form we find

\[-\frac{d[Cl]}{dt} = \frac{A_7 A_{12} A_{14} \exp\left(-\frac{E_7 + E_{12} + E_{14} - E_8 - E_{13}}{RT}\right)}{A_8 A_{13}} [Cl]^2 [M]\]

(16)
where $A$ represents the pre-exponential factors and $E$ the activation energies for the respective reactions. From a consideration of the reactions we may assume $E_7 = E_{12} = E_{14} = E_8 = 0$. $E_{13}$ however is at least equal to the ClM bond energy, hence

$$\frac{-d}{dt} \left[ \text{Cl} \right] = \frac{A_7 A_{12} A_{14} \exp \left(-E_{13}\right)}{A_8 A_{13}} \left[ \text{Cl} \right]^2 \left[ \text{M} \right]$$  \hspace{1cm} (17)$$

Calculation of the various $A$ factors shows the above combination to be of the correct order of magnitude ($10^{16}$ cm$^6$ moles$^{-2}$ sec$^{-1}$). The observed negative activation energy can be seen to be related to the bond energy of the stabilized ClM complex. In view of the relationship noted between the rate constants and the boiling points of the third bodies $^{18}$ Davidson $^{17}$ assumed the XM bonds were due to Van der Waal's forces. Porter $^{19}$ later suggested the bond could be the result of charge transfer. Absorption spectra attributable to such complexes have been observed in solution with organic third bodies as reported by Porter.

In the above discussions it has been assumed that $[\text{Cl}] \ll [\text{M}]$ which is usually the case at pressures of 0.5 at. at which flash photolysis systems are generally operated. If one could work with a system in which $[\text{Cl}] \geq [\text{M}]$ (low pressures), one would expect to observe
a change in the kinetics as certain of the gross inequalities are not longer true.

In mechanisms A and B the assumptions $k_2 \gg k_3 [M]$ and $k_8 \gg k_9 [Cl]$ respectively are still true and the observable kinetics remain

$$\frac{-d[Cl]}{dt} = k_{\text{obs}} [Cl]^2 [M] \quad (18)$$

In mechanism C, $k_8 \gg k_{12} [M]$ is still valid but $k_{13} [M] \gg k_{14} [Cl]$ may no longer hold true when $[Cl] \geq [M]$.

Under such circumstances the equilibrium conditions assumed for $[ClM]$ may no longer hold since reaction (14) becomes fast with respect to reaction (13). Reaction (12) then becomes rate determining and the observed kinetics would be

$$\frac{-d[Cl]}{dt} = k'_{\text{obs}} [Cl] [M]^2 \quad (19)$$

Thus, working at low pressures where $[Cl] \geq [M]$ it should be a simple matter to differentiate between mechanism C as opposed to mechanisms A or B being operative. No such obvious difference between A and B would be observed however.

To date no-one has been able to apply this simple mechanism test due to inherent limitations of the experimental
techniques available. In flash photolyses a high pressure of inert gas is necessary to prevent a temperature rise during recombination. Shock tubes employ a sudden high pressure and temperature to dissociate the gas and thus the method is dependent for its existence on the opposite circumstances we wish to achieve. It is to be noted also that both these techniques require an inert gas be added, further complicating elucidation of the kinetics in that M is now two species undissociated halogen and inert gas, with differing third body efficiencies.

Ogryzlo \(^{20}\) has shown that up to 50\% dissociation of Cl\(_2\) can be achieved with a microwave discharge at pressures below 1 mm Hg. Thus a determination of the rate constant for the recombination and a direct test of the "complex" mechanism is now conceivable.

d) Concurrent Recombination into Electronically Excited Molecular States

The above mechanisms describe the recombination of ground state atoms with the assumption that all collisions follow the potential energy curve for the ground electronic state of the molecule. The possibility that recombinations are occurring into electronically excited molecular states (with subsequent transition to the ground state) has not been considered to any great extent by most workers.
Figure I, though drawn for chlorine specifically, gives a simplified picture of the potential energy curves for the halogens in general. The Morse potential curves of Figure I were calculated from molecular constants given by Douglas et al. The ground state of all halogen atoms \((X)\) is the \(X(2P_{3/2})\). The first excited state in all cases is the \(X(2P_{1/2})\), the excitation energy varying greatly among the halogens. From absorption spectra it is known that various molecular states are possible from combinations of these atoms. With reference to Figure I it can be seen that the ground \(X_2(\Sigma_g^+)\) molecular state dissociates into two \(X(2P_{3/2})\) ground state atoms. Each halogen also has an \(X_2(3\Pi_{1u})\) state, indicated by the unlabelled, dotted curve, which dissociates into two ground state atoms. This is a repulsive state in chlorine but is a bound state in bromine and iodine. Each also has a bound \(X_2(3\Pi_{0u}^+)\) state which dissociates into a ground \(X(2P_{3/2})\) and an excited \(X(2P_{1/2})\) atom. A more complete list of the various states is given in Table II, taken from data by Muliken.

The only workers who have considered the possible importance of these upper states in the recombination reaction are Davidson and Rabinowitch. They point out that the halogen atom ground state \(2P_{3/2}\) is 4-fold degenerate.
Figure I. Morse Potential Energy Curves for Cl₂
## Table II

<table>
<thead>
<tr>
<th>Parity</th>
<th>State</th>
<th>Dissociation Products</th>
<th>Nature</th>
<th>Found In</th>
</tr>
</thead>
<tbody>
<tr>
<td>u</td>
<td>$^3\Sigma^+$</td>
<td>1</td>
<td>a b</td>
<td>repulsive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0$^-$</td>
<td>a b</td>
<td>&quot;</td>
</tr>
<tr>
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<td>$^1\Sigma^-$</td>
<td>0$^-$</td>
<td>a a</td>
<td>&quot;</td>
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<tr>
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<td>1</td>
<td>a b</td>
<td>&quot;</td>
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<td></td>
<td></td>
<td>2</td>
<td>a b</td>
<td>&quot;</td>
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</tr>
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<td>g</td>
<td>$^1\Sigma^+$</td>
<td>0$^+$</td>
<td>b b</td>
<td>&quot;</td>
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<tr>
<td></td>
<td>$^3\Sigma^-$</td>
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<tr>
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<td>$^1\Pi$</td>
<td>1</td>
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<tr>
<td></td>
<td>$^3\Pi$</td>
<td>0$^-$</td>
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<td>0$^+$</td>
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<td>$^1\Sigma^+$</td>
<td>0$^+$</td>
<td>a a</td>
<td>stable</td>
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</table>

a = X($^2P_{3/2}$)
b = X($^2P_{1/2}$)

* stable in Br$_2$ and I$_2$ and repulsive in Cl$_2$
Thus, the total degeneracy of a pair of recombining atoms is 16. Since the ground molecular state ($^1\Sigma_g^+$) is one-fold degenerate it may be that only $1/16$ of the collisions are favorable for recombination into a stable configuration. At present it is not possible to decide on the significance of this factor in theoretical considerations.

It is quite possible that recombination does occur into these excited molecular states. If so it should be possible to study recombinations of this type by the emission accompanying the electronic transition to the ground state is such processes occur.

Emission spectra attributed to excited $\rightarrow$ ground transitions from halogens in a heated vessel ($\approx 1200^\circ$K) have been reported $^{23,24,25,26}$. These usually consist of a continuum often accompanied by a band spectrum at low pressures. The various authors attribute the continuum to a two-body recombination which may be written

$$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2^*$$  \hspace{1cm} (2, 3)

$$\text{Cl}_2^* \rightarrow \text{Cl}_2 + h\nu$$  \hspace{1cm} (20)

The Cl$_2^*$ can result from combination along any of the potential energy surfaces, bonding or non-bonding.

Uchida $^{24}$, observing the spectra in a heated capillary, noted that spectra taken near the wall showed a band structure
and those near the center showed the continuum. A comparison of the bands with those obtained in absorption studies allowed him to identify the upper state as the $^3\psi_{0u}^+$ state shown in Figure I. He suggested that the wall acted as an energy sink, stabilizing the recombination of a $^2P_{3/2}$ and a $^2P_{1/2}$ atom into the $^3\psi_{0u}^+$ state. He also noted that the intensity of the band spectrum was proportional to the fourth power of the atom concentration as determined from degree of dissociation calculations at the temperatures used. Uchida proposed the following mechanisms to account for these observations.

$$3X(^2P_{3/2}) \longrightarrow X_2(^1\Sigma_g^+) + X(^2P_{1/2}) + KE \quad (21)$$

$$X(^2P_{3/2}) + X(^2P_{1/2}) + \text{wall} \longrightarrow X_2(^3\psi_{0u}^+) + \text{wall} \quad (22)$$

(where $X = \text{halogen}$)

One further point to be noted from these studies is that all workers conclude that the emitting species is formed by recombination of atoms. They all agree that the source of the emission is not produced by electronic excitation in a thermal process. Thus recombination into upper states must be considered in any study of recombination kinetics.
There is no reason to suppose that recombination into the bound upper states should follow a different mechanism from that into the ground state but different rate constants for each are conceivable. Depending on the method of production of the atomic species and the conditions present in the experimental system more or less recombination may take place into these upper states. A better knowledge of these processes may help reconcile the discrepancies between theory and experiment and give more conclusive proof for the validity of one of the reaction mechanisms.

e) Object of this Project

In this research it was found possible to generate, maintain and measure chlorine atoms in a low pressure flow system with an electrodless discharge, in sufficient concentration to study the kinetics of their recombination.

With this technique it was hoped to be able to calculate a value for \( k_{1M} \), which, as mentioned previously, is not well determined in the literature.

It was also hoped that mechanism breakdown would be observed at the low pressures possible in order to test the mechanistic proposals.

It was further hoped to observe and study the emission
due to recombination into an excited state of the Cl₂ molecule in order to help establish the role of these upper states in the recombination process.
MATERIALS AND EQUIPMENT

Chlorine from Matheson of Canada Ltd., Whitby, Ont. (99.5% min. purity) was used directly from the cylinder. A sample of this chlorine was purified by a series of trap to trap distillations in vacuum (the first and last fractions being discarded), and showed no difference in behaviour from that used directly.

The NOCl used for titration of the Cl atoms was from Matheson (93.0% min. purity) which was purified by trap to trap distillations as above and stored in a 15 l. bulb. Its purity was checked by its infrared absorption spectra in comparison with spectra published in the literature (27) until peaks attributed to NO and NO₂ decreased to a point where the NOCl was 98+% pure. NOCl samples were drawn directly from the storage bulb and compared with samples from the pump trap which had passed through the system (needle valve, stopcocks etc.) and showed that the latter had suffered little or no decomposition.

The H₃PO₄ used as poison was B.D.H. Analar Orthophosphoric acid, diluted to 20% by volume with distilled water before coating on the reaction tube. The tube was washed with hot, concentrated NaOH and rinsed well with water before poisoning.

The concentrated H₂SO₄, di-n-octyl phthlate, and Hg used in the flowmeters was dried and degassed thoroughly by heating under vacuum.
Dissociation of the chlorine was achieved with a Raytheon Microwave Generator, operating at 2450 Mc/sec, with a maximum power output of 100 watts. The gas discharge was initiated by a tesla coil spark and was operated at about 60% power output.

The resistance bridge circuit was constructed to our specifications by the U. B. C. electronics technician and a Tinsley potentiometer was used for potential measurements.

The detector coil was made of pure Pt wire (0.015" dia.) about 36 in. in length, wound into a tight spiral to a length of about 2 in. then coiled to fit the inside of the reaction tube. It was coated by electroplating Ni from a basic Nickel Ammonium Sulphate solution.

Kel-F No. 90 fluorocarbon grease (3-M Company) was used exclusively for all stopcocks and joints.
EXPERIMENTAL PROCEDURE

a) Flow System

A somewhat schematic diagram of the apparatus is shown in figure II.

The inlet tubes A and B were connected directly to bubblers which ensured that the gas entering the system was at a constant back pressure of one atmosphere. Inlet C, in parallel with A connected with a 22 litre storage bulb of purified chlorine. A Fisher-Porter glass-teflon needle valve was used to control the chlorine flow.

The flowmeters \( F_1, F_2, \) and \( F_3 \), containing \( \text{H}_2\text{SO}_4 \), \( \text{H}_2\text{SO}_4 \) and \( \text{Hg} \) respectively as manometer liquids, measured the pressure difference across a fine capillary as the gas flowed through it. The flowmeters were calibrated in moles/sec flow as a function of manometer deflection by trapping and weighing condensable materials or by measuring the volume of exhaust gas from the pump for a timed run. Ideal gas laws were then used to calculate the flow.

Flowmeter \( F_1 \) had two capillaries which could be used individually or in parallel, increasing the useful range of the meter. Flowmeter \( F_3 \) was used to measure bulk
Figure II. Flow System
quantities of non-corrosive gases and admit them to the system before or after the discharge tube DT. Flowmeter $F_2$ was used for measuring smaller flows (of the order of $0$ to $10 \mu$ moles/sec) for gas titrations through the titration head (inset T).

The rack and pinion system by which the detector D was moved in the reaction tube is indicated by R. The pinion gear was sealed into a B-19 ground joint which allowed it to be rotated moving the rack supporting the detector, while the system was under vacuum.

The constriction shown between the reaction tube and the trap was necessary to slow down the flow so that optimum decay in the reaction tube was achieved.

In operation the principle flow was from left to right as pictured. Chlorine from the storage bulb C or from the tank through inlet B was controlled by the glass-teflon valve and its flow measured by $F_1$. It then flowed through the 2450 Mc/sec microwave discharge region DT which was cooled by a blast of compressed air. The atom/molecule stream flowed down the reaction tube RX past the moveable detector D. The chlorine was condensed out of the gas stream in a wide bore U-tube trap maintained at $-176^\circ$ C in liquid nitrogen.
Pressure measurements on the system were made with a tilting McLeod gauge (not illustrated) connected at M. The gauge was first filled with a backing pressure of helium which was allowed to come to equilibrium with the chlorine system since chlorine would react with the mercury of the gauge. A flow vs pressure calibration graph was drawn so that the time consuming pressure measurements need not be taken for each run with the attendant danger that conditions in the system had changed before or during the pressure measurement.

b) Surface Poisoning

Previous workers, notably Rodebusch \(^{(2)}\) and Schwab \(^{(4)}\), generating chlorine atoms with an electrode type electric discharge, found that the atoms recombined very rapidly on the quartz or pyrex walls of the reaction vessel and could not be maintained for more than 1 cm in the flow system. They calculated a wall recombination coefficient \(\gamma\) (defined later) of \(10^{-1}\), meaning that one atom-wall collision in 10 result in recombination. It has been found by Ogryzlo \(^{(28)}\) of this laboratory that certain non-metallic oxy-acids, when coated on the walls of the reaction tube can reduce \(\gamma\) to about \(10^{-5}\) (1 collision in \(10^5\) effective in recombination) permitting chlorine atom flows to be maintained for a considerable distance in the flow system. Phosphoric acid "poison" (hereafter used without quotations) was used exclusively in this work.
The poison was applied by filling the reaction tube (previously cleaned with hot conc. NaOH and rinsed well with water) with a 20\% by volume solution of $\text{H}_2\text{PO}_4$, draining and removing excess water by evacuation. The discharge tube was dried before each series of runs by discharging pure helium with little cooling air until the discharge glow was pure white (He) rather than pink ($\text{H}_2\text{O}$).

c) Production of the Atomic Species

In the design and construction of the flow system a number of requirements had to be met to ensure optimum conditions for the measurement of the atom decay.

The atom concentration had to be large enough to be detected - at least $10^{-9}$ moles/cc. This was easily achieved by the 2450 Mc/sec microwave discharge. A "light source"\(^{(29)}\) type discharge cavity was found to have a rather small pressure range in which the discharge could be initiated. An open "C" type discharge head was found to give a good atom concentration over a wide range of operating pressures (0.2 to 2.0 mm Hg). The pressure in the system had to be low enough to maintain the atom stream in the tube, that is the decay had to be reasonably slow. On the other hand it had to be high enough to allow a reasonable
decay to occur in the length of the reaction tube (≈ 30 cm). Moreover, the pressure has a great effect on the velocity of the flow. With a very fast flow the atoms may be swept past the detector unmeasured, with a slow flow the recombination will have gone to completion before the detector is reached.

Since the chlorine pressure is reduced effectively to zero at the liquid N\textsubscript{2} trap, very rapid flow occurs, with the difficulty mentioned above. The pressure can be increased and the flow diminished by addition of an inert non condensable gas. This however would introduce another third body into the reaction scheme and complicate the kinetics. It is also found that while the total pressure can be varied by the addition of an inert gas, the concentrations of Cl\textsubscript{2} and inert gas are not independently variable. At a constant Cl\textsubscript{2} flow, variation of the pressure by changing the inert gas flow also changes the Cl\textsubscript{2} concentration.

It was found that the system could be operated using pure chlorine by slowing the flow thus raising the pressure. An air bleed installed past the liquid N\textsubscript{2} trap achieved this by introducing a non zero pressure at the trap but the effect was found to be somewhat erratic and non-reproducible. This technique also suffered from the possibility of back diffusion from the air bleed into the system.
As an alternative, a constriction was placed in the system just before the liquid $N_2$ trap and adjusted to achieve the optimum conditions as described. This method had the added advantage that a flow-pressure calibration could be made to obviate the necessity of pressure measurements while operating, as described previously.

In the early stages of the project, a simple U-tube trap in liquid $N_2$ was used to condense the chlorine. This was found to fill up rather rapidly and gradually alter the conditions in the system. An extremely wide bore trap could not be used since it was feared that a $Cl_2$ "fog" would form at the center and be swept through to the pump. A compromise was struck with a trap consisting of a wide entrance arm and a narrow exit arm. This type of trap is only useful when the gas flow is mainly condensable. If large flows of non-condensable gases are used the narrow exit arm restricts the flow through the trap and builds up a pressure in the system much the same as the constriction.

Control of flows within the system is also a difficulty in the case of corrosive gases. Chlorine immediately attacked the moving parts of any metallic valve, particularly the needle and seat, causing erratic, non-reproducible flows and forming volatile metallic chlorides. A network
of capillary flow controls coupled with control of the Cl₂ back pressure by various freezing baths (chlorine from the storage bulb) was somewhat better but still unsatisfactory. A needle valve consisting of a glass seat and a teflon needle (commercially available only quite recently), while not giving very fine control, gave a steady flow and was used in all runs in this work.

d) Atom Detection and Measurement

The atoms flowing in the reaction tube were measured by an "isothermal calorimetric atom detector" as described previously by Ogryzlo \(^{(20)}\) and Schiff et al \(^{(30)}\). This detector consists of a helically wound spiral of platinum wire electroplated with nickel and movable under vacuum along the reaction tube (RX) by the rack and pinion gear system (R). The Pt wire formed one resistance arm of the Wheatstone bridge circuit shown in figure (III).

With the discharge off i.e. no atoms flowing, current is passed through the detector and the bridge balanced by adjusting the current and/or the resistance of the decade resistance box. The current through the detector is then measured on an accurate potentiometer by measuring the potential drop across the 1 ohm precision resistor. With the microwave discharge on and atoms present, the atoms
Figure III. Circuit Diagram of Detector Bridge
P potentiometer terminal
C common
G galvanometer
T tapping key
recombine on the surface of the Ni/Pt coil releasing 29 kcal/mole \( \left( \frac{1}{2} D(\text{Cl-Cl}) \right) \) in the form of heat. For the bridge to be balanced under these conditions the current through the detector must be decreased, returning the coil to its original temperature and thus its original resistance. From the magnitude of the decrease of the squares of the currents, \( \Delta (i_2^2) \), the atom flow incident on the detector could be calculated by the formula

\[
\text{atom flow} = \frac{\Delta (i_2^2) R}{4.18 \frac{D}{2}} = \frac{g \text{ atom}}{\text{sec}}
\]

where \( \Delta (i_2^2) \) is the current squared decrease \( = (i_1^2) - (i_2^2) \)

\( R \) is the resistance of the detector

\( D \) is the dissociation energy of the bond being formed

4.18 is the electrical power to heat conversion factor

The concentration of gas in the system can be calculated from the ideal gas laws (which are valid for this work) where

\[
\text{concentration} = M = \frac{n}{V} = \frac{P}{RT} \frac{\text{moles}}{\text{cm}^3}
\]

where

\( n \) is the number of moles

\( V \) is unit volume
P is the pressure as measured by the tilting McLeod gauge

R is the gas constant

T is the absolute temperature

The concentrations of various species in the system can be calculated assuming a linear contribution to the concentration by the flows of the respective species as measured by the flowmeters or the detector.

At the pressures encountered in the system the flow can be assumed to be linear (diffusion, viscosity etc. negligible), thus the velocity can be calculated by the formula

\[ \frac{f}{[M] \pi r^2} = \frac{cm}{sec} \]  

(25)

where 
\[ [M] \] is as calculated above
\[ \pi r^2 \] is the cross sectional area of the tube in which the gas is flowing
\[ f \] is the flow in moles/sec determined from the calibrated flowmeters.

The reaction time in the system is then simply the distance from an arbitrary zero to the point of measurement, divided by the velocity.

e) Detector Efficiency

The efficiency and accuracy of the detector were checked
by a gas titration procedure described by Ogryzlo (20) employing the fast reaction $\text{NOCl} + \text{Cl} \rightarrow \text{NO} + \text{Cl}_2$. The atom concentration at the titration inlet ($T$, figure II) was measured by the detector. Then, using the detector only as a qualitative atom detection instrument, NOCl was added till no atoms were detectable. Figure (IV) shows a plot of $\Delta (i^2)$ against NOCl flow. The sharp break in the plot corresponds to the titration end point. This would be expected to occur at $\Delta (i^2) = 0$, however the changing concentrations of the various species (NOCl, Cl$_2$, NO) changes the heat capacity of the flow stream slightly and the detection system is no longer strictly isothermal. The arrow on the abscissa of figure IV corresponds to the atom flow as measured by the detector, the correspondence with the titration end-point is easily seen.

With the discovery of the emissive glow, detector efficiency was easily checked by noting whether the detector was killing the glow, i.e. destroying all the atoms. The titration procedure outlined above was still necessary, however, to ensure that only atoms and not spurious energetic species from the discharge were being detected.

f) Emission Studies, Spectroscopy

The spectroscopic studies were conducted using a portable
Figure IV. NOCl Titration of Cl Atoms
reaction system similar to the flow system described above. The reaction tube in this system had an optical window at one end (the atom stream entering through a "T" joint) allowing the spectrograph to be directed along the tube to achieve a long light path. The reaction tube was poisoned as described above and coated on the outside with a magnesium oxide "paint" to increase the light intensity within the tube.

The emission spectrum of Neon has a number of intense lines in the region between 5400 and 10,000 Å, and was used as a reference calibration source in all cases.

Spectra were photographed on the Jarrell-Ash f 6.3 grating spectrograph requiring exposures of one to three hours on Kodak 103 F or 1 N spectroscopic plates.

g) Emissive Decay

In the absence of a photoelectric detection system suitable for application on our system, a photographic method of measuring the decay of the emissive glow had to be devised.

This consisted of focussing a camera (Konica 35 mm, 135 mm telephoto lens) on the glow in the reaction tube of the main flow system and photographing the emission. The film was then scanned by a densitometer as shown in figure V where
Figure V. Densitometer Scan of Emissive Decay Photograph
optical density (which will be related to emission intensity) is plotted against reaction tube position.

This process is very dependent on the handling of the film (developing, fixing etc.) and no standard calibration relating optical density (O.D.) to emission intensity could be made. Rather a calibration had to be made for each film. This consisted of taking a series of exposures of varying times of the same emission and plotting exposure time against O.D. for a given position in the tube. This gave a "characteristic curve" which is shown in figure VI. Since the number of quanta incident on the film from a constant source is proportional to the exposure time a relative quanta (hν) scale could be superimposed on the exposure time axis. Thus the optical density at any position in any run could be assigned a relative $h\nu$ value from the calibration graph and $dh\nu/dt$ determined.

From photographs of a constant light source with an ordinary lens it was found that the recorded intensity decreased toward the edges of the picture in accord with the distance-intensity laws of optics. To minimize this effect it was desirable to photograph the system from as far away as possible, thus requiring the 135 mm telephoto lens to maintain an adequate image size.
Figure VI. "Characteristic Curve" of Film Relating Optical Density to Emission Intensity
Since the greater part of the emission was in the infrared a special high speed infrared film was used (Kodak HIR-417). The film was still somewhat sensitive to visible and UV radiation however and an elaborate system of light traps was built to prevent light from the discharge being "piped" along the reaction tube. In spite of the light traps it was found that some visible and ultraviolet radiation was being photographed necessitating a red filter on the camera lens (Corning #2408) which cut off all radiation with wavelength shorter than 6250 Å.
RESULTS AND DISCUSSION

a) Treatment of Kinetic Data

Figure VII shows the observed decay of chlorine atoms in the system as a plot of $[\text{Cl}]$ against time. It is apparent in these plots that the decay rate varies with pressure, that is, there is a dependence on the third body concentration $[\text{M}]$.

If the recombination proceeds solely as indicated by

$$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \quad (1)$$

that is,

$$-\frac{d[\text{Cl}]}{dt} = k_{1\text{M}} [\text{Cl}]^2 [\text{M}] \quad (1a)$$

da plot of $1/[\text{Cl}]$ against time should yield a straight line as indicated by integration of eqn. (1a). Figure VIII shows no such linear dependence and it is obvious that equation (1) does not fully explain the decay.

As discussed previously, if mechanism C were operative and the low pressure "breakdown" or transition in kinetic order, was being observed, the kinetics would be given by,

$$-\frac{d[\text{Cl}]}{dt} = k_{\text{obs}}[\text{Cl}][\text{M}]^2 \quad (19)$$

(where $k_{\text{obs}} = \frac{k_7 k_{12}}{k_8}$), that is first order in $[\text{Cl}]$.

Integration of (19) indicates that a plot of $\ln [\text{Cl}]$ against
time should result in a straight line of slope $k_{obs} [M]^2$. This plot is shown in figure IX. The straight line plot again is not observed, rather there is a slight curvature in a direction which would indicate a higher order in $[\text{Cl}]$ decay.

The findings of figures VIII and IX together indicate that the decay is either of a fractional order in $[\text{Cl}]$ or consists of concurrent first and second order $[\text{Cl}]$ decays.

The above discussion has, however, ignored heterogeneous recombination on the walls of the reaction vessel. As noted previously it was necessary to poison the walls of the reaction tube with $\text{H}_3\text{PO}_4$ to prevent, or at least retard, surface recombination. In studies on the recombination of other atomic species e.g. $\text{H}$, $^{31}\text{N}$, $^{32}\text{O}$, $^{30}\text{O}$ etc. it has been ascertained that in all cases the wall recombination is first order in the atomic species. This knowledge, coupled with the fact that the bulk of the recombination is first order in $[\text{Cl}]$ (as evidenced by the "almost" straight lines of graph IX) leads us to suspect that a first order wall decay must be accounted for before the gas phase reaction can be investigated. This surface recombination may be written

$$\text{Cl} + \text{wall} \rightarrow \frac{1}{2}\text{Cl}_2 + \text{wall} \quad (26)$$

where $k_{26}$ is the first order wall recombination rate constant.
Figure VII. $[\text{Cl}]$ against time

Figure VIII. $1/[\text{Cl}]$ against time

Figure IX. $\log [\text{Cl}]$ against time

- $\times$ - high pressure
- $\circ$ - low pressure
The reactions which we will assume to occur are

\[ \text{Cl} + \text{wall} \rightarrow \frac{1}{2}\text{Cl}_2 + \text{wall} \]  \hspace{1cm} (26)

and  \[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \]  \hspace{1cm} (1)

with the resultant rate equation

\[ -\frac{d[\text{Cl}]}{dt} = k_{26} [\text{Cl}] + 2k_{1M} [\text{Cl}]^2 [\text{M}] \]  \hspace{1cm} (27)

assuming no mechanism breakdown has occurred.

Integration of equation (25) between appropriate limits results in

\[ k_{26} t = \ln \left( \frac{k_{26} + 2k_{1M} [\text{Cl}_t] [\text{M}]}{[\text{Cl}_0]} \right) \]  \hspace{1cm} (28)

which can be rearranged to

\[ k_{1M} = k_{26} \left( \frac{1}{[\text{Cl}_t]} - \frac{1}{[\text{Cl}_0]} \right) \left( \text{antilog} \frac{k_{26} t}{2.303} - 1 \right) \]  \hspace{1cm} (29)

The desired rate constant, \( k_{1M} \), is seen to be given only in terms of the other unknown constant, \( k_{26} \). In order to determine \( k_{26} \) so that \( k_{1M} \) may be calculated, a different treatment of the integrated expression, equation (28), must be used.
If we take the exponential of both sides of equation (28), expand \( \exp(k_{26}t) \) as 

\[
1 + k_{26}t + \frac{(k_{26}t)^2}{2!} + \ldots
\]

terminating the series at \( 1 + k_{26}t \), a simpler expression results. This series termination is justifiable in our experiment where \( k_{26} \) is found to be of the order of \( 4 \ \text{sec}^{-1} \) and \( t \) of the order of \( 5 \times 10^{-2} \ \text{sec} \). Thus the series is

\[
1 + 0.20 + 0.02 + \ldots
\]

Equation (28) then becomes

\[
1 + k_{26}t = \left( \frac{k_{26} + 2k_{1M}[M][Cl]_t}{k_{26} + 2k_{1M}[M][Cl]_o} \right) \frac{[Cl]_o - [Cl]_t}{t[Cl]_t}
\]

which rearranges to

\[
k_{26} + 2k_{1M}[M][Cl]_o = \frac{[Cl]_o - [Cl]_t}{t[Cl]_t}
\]

Thus a plot of the right hand side of equation (31) against \( 2 [M][Cl]_o \) should, if our mechanism is correct, result in a straight line of slope \( k_{1M} \) and intercept \( k_{26} \). This plot is presented in figure X. \( k_{1M} \) may be taken from the slope of figure X or may be calculated using equation 29 in which \( k_{26} \) is taken from the intercept of figure X.

A reaction scheme based on the assumption of a transition in kinetic order at low pressures, that is wall
Figure X. $\frac{[\text{Cl}]_o - [\text{Cl}]_t}{t[\text{Cl}]_t}$ against $2[M][\text{Cl}]_o$.
recombination concurrent with gas phase recombination via the low pressure case of mechanism C, results in the kinetic expression

\[
\frac{-d[C_1]}{dt} = k_{26} [C_1] + k_{32} [C_1][M]^2
\]  
(32)

This, however, is unsatisfactory since it does not account for the curvature in figure IX which indicates a higher order \([C_1]\) dependence.

It is possible that only a partial low pressure transition of mechanism C occurs, in which case the kinetic expression would be

\[
\frac{-d[C_1]}{dt} = k_{26} [C_1] + \frac{k_7 k_{12} k_{14} [C_1]^2 [M]^2}{k_8 (k_{13} [M] + k_{14} [C_1])}
\]  
(33)

which is impossible to integrate simply and treat as we did equation (27). Moreover, the data is not sufficiently accurate to test for only a partial kinetic transition particularly since at the low pressures required to observe the transition the first term of equation (33) (wall decay) is dominant.

If mechanism breakdown has not occurred the results can be interpreted to indicate that the kinetics proposed by equation (27) are essentially correct, that is, the
reaction can be represented by

\[ \text{Cl + wall } \rightarrow \frac{1}{2}\text{Cl}_2 + \text{wall} \quad (26) \]

and

\[ \text{Cl + Cl + M } \rightarrow \text{Cl}_2 + \text{M} \quad (1) \]

The scatter in the points of figure X can be attributed to experimental error or may be ascribed to minor variations in poison efficiency. These points represent a series of seventeen runs conducted over a period of about a week without re-poisoning the reaction tube. It was, however, opened to the atmosphere on various occasions and despite thorough degassing the poison may have absorbed water vapor etc. which could have changed its efficiency. Each point would then be on a line parallel to that indicated having a slightly different intercept. The \( k_w \) arrived at in figure X is then the best value available from the data.

The slope of figure X gives a value for \( k_{LM} \), however, due to the scatter, it was considered best to calculate \( k_{LM} \) from equation (29) using the \( k_{0P} \) from figure X. The results of these calculations are given in Table (III) together with other pertinent data for the individual runs.
Table III

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<tr>
<td>0.45</td>
<td>0.36</td>
<td>1.36</td>
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</tbody>
</table>

$\text{av 2.45}$
With \( k_{1M} = k_{1Cl_2} \) determined in the above manner in a system of pure chlorine, the rate constants for other third body gases may similarly be determined by adding these gases to the \( Cl_2-Cl \) atom stream.

With the addition of helium, for instance, \([M]\) in all equations must now be written \([M]_{\text{Total}} = [Cl_2] + [He]\). If we assume a linear relationship between the recombination reactions the rate equation previously given by reaction (27) becomes

\[
\frac{-d[Cl]}{dt} = k_{26} [Cl] + 2k_{1Cl_2} [Cl]^2 [Cl_2] + 2k_{1He} [Cl]^2 [He]
\]

(35)

and equation (31) becomes

\[
k_{26} + 2(k_{1Cl_2} [Cl_2] + k_{1He} [He])(Cl)_o = \frac{[Cl]_o - [Cl]_t}{t [Cl]_t}
\]

(36)

and a plot of \( \frac{[Cl]_o - [Cl]_t}{t [Cl]_t} - 2k_{1Cl_2} [Cl_2] [Cl]_o \) against \( 2[He][Cl]_o \) should yield a straight line of slope \( k_{1He} \), intercept \( k_{26} \) (which should be unchanged). This plot is shown in figure XI.

Table IV summarizes the rate constants obtained from the above calculations and graphs and includes comparisons.
Figure XI. \[ \frac{[\text{Cl}]_0 - [\text{Cl}]_t}{t [\text{Cl}]_t} - 2k_{1\text{Cl}_2}[\text{Cl}_2][\text{Cl}]_0 \]

\[ = \emptyset \text{ against } 2[H_e][\text{Cl}]_0 \]
<table>
<thead>
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<th>Constant</th>
<th>Method</th>
<th>Value</th>
<th>Ref.</th>
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</thead>
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<td>Intercept of graph (VII)</td>
<td>3.90 s$^{-1}$</td>
<td>this work</td>
</tr>
<tr>
<td>$k_{26}$</td>
<td>&quot; (VIII)</td>
<td>3.90 s$^{-1}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$k_{26}$</td>
<td>Similar flow system</td>
<td>2 s$^{-1}$</td>
<td>(28)</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Slope graph (VII)</td>
<td>$2.75 \times 10^{16}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>this work</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Average of calculations using eqn (29), $k_w = 3.9$ s$^{-1}$</td>
<td>$2.45 \times 10^{16}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Shock tube (extrapolated to 40°C)</td>
<td>$3.30 \times 10^{16}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>(10)</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Unspecified</td>
<td>$2.0 \times 10^{16}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>(11)</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Chlorination of CO (300°C)</td>
<td>$5.6 \times 10^{15}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>(12)</td>
</tr>
<tr>
<td>$k_{1Cl_2}$</td>
<td>Photochlorination of hydrocarbons (40°C)</td>
<td>$6.5 \times 10^{17}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>(9)</td>
</tr>
<tr>
<td></td>
<td>(62°C)</td>
<td>$7.2 \times 10^{17}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
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<tr>
<td>$k_{1He}$</td>
<td>Chlorine Atom Recombination</td>
<td>$3.0 \times 10^{15}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>this work</td>
</tr>
<tr>
<td>$k_{1Ar}$</td>
<td>Bromine Atom Recombination</td>
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<td>(15)</td>
</tr>
<tr>
<td>$k_{1He}$</td>
<td>Iodine Atom Recombination</td>
<td>$1.5 \times 10^{15}$ cm$^6$ moles$^{-2}$ s$^{-1}$</td>
<td>(12)</td>
</tr>
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</table>
with rate constants for analogous reactions in I and Br atom recombination.

In this study all rate constants were determined at 40°C. The temperatures for the other rate constants are noted in Table IV where these are known.

b) Discussion of Rate Constants

As can be seen from Table IV the results obtained in this work compare favourably with the results of Martens (11) assuming he has defined the rate constant in the same manner. (The convention used in this work is that the rate equations for reaction (1) be written

\[ \frac{-d[Cl]}{dt} = 2k_{1M} [Cl]^2 [M] \]

the factor 2 appears because two chlorine atoms are removed by the reaction. Some workers however write this as

\[ \frac{-1}{2} \frac{d[Cl]}{dt} = k'_{1M} [Cl]^2 [M] = \frac{d[Cl_2]}{dt} \]

depending, it would appear, on whether chlorine atom decay or molecule formation is being measured. It is easily seen that \( k'_{1M} = 2k_{1M} \).

The value quoted in Table IV for Hardwick and Hirakawa's (10) work was calculated from an empirical equation determined
at about $1600^\circ K$ which may not hold over all temperature ranges. The close agreement is, nonetheless, encouraging.

The values given by Dainton et al.\(^{(9)}\) are seen to be greater by a factor of 20. In their work, however, it may be that they did not adequately account for wall recombination. They maintain that at the high chlorine pressures used (400 mm Hg), and irradiation only at the center of their vessel, diffusion of chlorine atoms to the wall is negligible. They base this on an assumed diffusion velocity and lifetime for the Cl atom. If their assumed Cl atom lifetime is calculated to be consistent with their high rate constant, they have assumed too short a lifetime for Cl. That is, a longer lived Cl atom is more likely to diffuse to the wall. From the noted efficiency of wall recombination in an unpoisoned system neglect of this effect may account for their high values of $k_{1M}$.

One further point which casts doubt on the reliability of their results is the positive temperature coefficient they observe when all other atom recombinations have been shown to have a negative temperature dependence.

The low pressure transition in kinetic order anticipated, assuming complex mechanism C is operative in the recombination, was not observed. It was postulated that the order of
the observed kinetics was dependent on the relative magnitudes of $k_{13}[M]$ and $k_{14}[Cl]$ in the reactions

$$M + ClM \rightarrow ClM* + M \quad (13)$$

and

$$Cl + ClM \rightarrow Cl_2 + M \quad (14)$$

For $k_{13}[M] \gg k_{14}[Cl]$ no breakdown would be observed and the gas phase decay could be expressed by

$$\frac{-d[Cl]}{dt} = k_{obs}[Cl]^2[M].$$

For $k_{13}[M] \ll k_{14}[Cl]$ the kinetic expression would be

$$\frac{-d[Cl]}{dt} = k_{obs}[Cl][M]^2,$$

having occurred.

A more detailed analysis of this question, based on actual experimental conditions indicates that our conditions were not adequate to effect the complete breakdown.

In general it was found that $[M] \approx 10[Cl]$. Thus, to effect the breakdown ($k_{14}[Cl] \gg k_{13}[M] \approx 10k_{13}[Cl]$), $k_{14}$ would have to be at least 10 times larger than $10k_{13}$ (i.e. $k_{14} \approx 100k_{13}$). The activation energy of reaction 13 is at least equal to the stabilization energy of the ClM complex (approximately 1 kcal mole$^{-1}$). The activation energy for reaction 14 need only be a small fraction of this, and the resultant difference in rate constants is such that $k_{14} \approx 10k_{13}$, not $100k_{13}$ as required. Thus our experiment could only approach the breakdown point (if such a point exists) and no positive indication of mechanism breakdown would be observed.
It is possible that for experiments with lowest \([M]\) and highest \([Cl]\), the breakdown point was approached. This might account for some of the scatter in the experimental points of figure X.

c) \(Y\)

The coefficient of wall recombination, \(Y\), mentioned previously is defined as

\[
Y = \frac{2rk_w}{\left(\frac{8RT}{m}\right)^{3/2}} \tag{37}
\]

where \(r\) is the radius of the reaction tube

\(k_w\) is the wall recombination rate constant determined above

\[
\frac{8RT}{m} \tag{3/2}
\]

is the r.m.s. velocity of particles of mass \(m\) at temperature \(T\).

It represents the fraction of collisions with the wall which result in recombination.

The value for \(Y\) calculated from \(k_w = 3.9\ \text{sec}^{-1}\), \(r = 0.95\ \text{cm.}\), \(m = \text{Cl}\) atomic mass, at \(T = 313^\circ\text{K}\) is \(Y = 6.81 \times 10^{-5}\), that is, one collision in \((6.81 \times 10^{-5})^{-1} = 1.47 \times 10^4\) results in a recombination. Schwab \(^5\) reported that the surface recombination reaction occurred on almost every
collision in his system ($\gamma \approx 1$). The necessity and efficiency of the HgPO$_4$ poison used in this work is clearly demonstrated by comparison of these figures.

d) Spectroscopy

As discussed previously, recombination into electronically excited molecular states should be detectable by the emission accompanying the transition to the ground molecular state. After the mechanics of running pure Cl$_2$ had been perfected it was noted in a darkened room that the recombination within the reaction tube was accompanied by a weak, orange-red emission. Examination of this on a low dispersion glass prism spectrometer showed this emission to have a banded spectrum, extending from about 5400 Å into the infrared, well beyond the sensitivity limits of both the RCA 7102 photomultiplier tube (figure XII) and Kodak N film.

A photograph of the emission taken on a Jarrell-Ash grating spectrograph is shown in figure XIII where some band sequences are marked.

A number of workers had previously noted a band spectrum in Cl$_2$, both in absorption ($^{21, 22}$) and emission ($^{23, 24}$) between about 4000 and 6000 Å. They attributed this spectrum to a $^3\Pi_{0u^+} \rightarrow ^1\Sigma_g^+$ transition. Comparison of our spectrum with that reported by Uchida (in the 5500 to 6000 Å region) showed a marked correlation with a number
$^{3}P_{0}^+ \rightarrow ^{1}Σ_{g}^+$ Band Spectra

Figure XII. on Low Dispersion Glass Prism Instrument
RCA 7102 Photomultiplier Tube
Sensitivity given by dotted curve

Figure XIII. on Jarrel-Ash f6.3 Grating Spectrograph
Kodak 103aF plates
Cl$_2$ spectrum 60 min, slit 50 μ
Ne reference 25 sec, slit 15 μ
Cl₂ \textcolor{red}{3Π_{0u}^+} \rightarrow \textcolor{blue}{\Sigma_{g^+}} \quad \text{Spectrum}

Ne reference
of band heads. Comparison of the frequency of our observed band heads with frequencies calculated for a $^3\Pi_{\text{Ou}^+} \rightarrow ^1\Sigma_g^+$ transition (from Douglas et al. [21]) is given in Table V where the calculated frequencies are given in brackets. It is obvious from this table that the emission indeed results from the $^3\Pi_{\text{Ou}^+} \rightarrow ^1\Sigma_g^+$ transition.

Two possible sources of the $^3\Pi_{\text{Ou}^+}$ excited molecular state are conceivable. It may be formed in the discharge region in which instance no consistent relationship between the emission intensity and the atom concentration should be noted. The excited state may also be formed in an atomic recombination reaction. In this case some relationship between atom concentration and emission intensity would be expected.

Using the photographic technique described in the Experimental Procedure it was possible to compare the decay of the emission intensity ($I$) with the Cl atom decay and determine whether there was a relationship between them. Assuming the arbitrary relation

$$I = k_e [\text{Cl}]^n [M]^m$$  \hspace{1cm} (38)

and noting that $M$ is constant within any given run, it can be seen that a plot of log $I$ against log $[\text{Cl}]$ should result in a straight line of slope $n$ (from the expression $\log I = n \log [\text{Cl}] + \text{const}$). This is shown in figure XIV from which $n = 2$. 
<table>
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<th>4</th>
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<th>8</th>
<th>9</th>
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</table>
Figure XIV. Log I against log [Cl]
Having thus determined that \( I \propto [Cl]^2 \) we can eliminate the possibility that the \( Cl_2(3\pi_{0u}^+) \) molecule is generated in the discharge, and conclude that it is formed by some atom reaction.

To investigate the third body dependence of the recombination to the \( 3\pi_{0u}^+ \) state we may compare two runs at different pressures (different \([M]\)). We wish to determine the order of reaction \( (m) \) with respect to \([M]\) in the formula

\[
I = k_e [Cl]^2 [M]^m \tag{38a}
\]

For two runs at different \([M]\) we may write

\[
\frac{I_1}{I_2} = \frac{[Cl]^2_1 [M]^m_1}{[Cl]^2_2 [M]^m_2} \tag{39}
\]

or

\[
\left( \frac{I_1}{[Cl]^2_1} \right) \left( \frac{[Cl]^2_2}{I_2} \right) = \left( \frac{[M]^m_1}{[M]^m_2} \right) \tag{40}
\]

With \( I \) and \([Cl]\) determined for a number of positions along the tube in each run, the value of the left hand side of equation (40) may be calculated. These values are shown in Table (VI) in a matrix notation which gives the appropriate \( I/[Cl]^2 \) ratio for all positions in one run, multiplied by all positions in the second run.
Table VI

\[
\left( \frac{I_1}{[Cl]_1^2} \right) \left( \frac{[Cl]^2}{I_2} \right)
\]

<table>
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<tr>
<th>Run 1</th>
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<td>2.55</td>
<td>2.45</td>
<td>2.43</td>
</tr>
</tbody>
</table>

average = 2.26

Run 1 \([M]_1 = 8.25 \times 10^{-3} \text{ moles/cm}^3\)

Run 2 \([M]_2 = 3.33 \times 10^{-3} \text{ moles/cm}^3\)

\[
\left( \frac{[M_1]}{[M_2]} \right)^m = 0
\]

\[
\left( \frac{[M_1]}{[M_2]} \right)^m = 1
\]

\[
\left( \frac{[M_1]}{[M_2]} \right)^m = 2.47
\]

\[
\left( \frac{[M_1]}{[M_2]} \right)^m = 6.1
\]
From Table VI it can be seen that \( m = 1 \), that is, first order in \([M]\) agrees well with observation. Thus the emission kinetics can be written

\[
I = k_{41} [Cl]^2 [M]
\]

(41)

similar to the gas phase recombination observed for recombination into the ground state.

The graphical and numerical arguments employed above to establish the \([Cl]^2\) and \([M]\) dependence do not exhibit the exact agreement that might be hoped for. Both are dependent on the photographic method of \( I \) determination. This method involving time exposures, film developing, densitometer traces and calibration graphs is subject to a number of random and cumulative errors and the agreement is exceptional, considering these factors.

With reference to the potential energy curves of figure I it can be seen that the \( ^3\Pi_{0u}^+ \) state does not correlate with ground state atoms. There are two possible methods of formation of the \( ^3\Pi_{0u}^+ \) state both, however, resulting in the same observable kinetics. The excited molecular state may be formed directly by recombination of a ground and an excited atom or may be formed by an intersystem crossing during the recombination of two ground state atoms.

The electron spin resonance spectrum obtained by McKenzie (33), with a Cl atom stream similar to ours,
suggests normal thermal equilibrium concentrations of ground and excited Cl atoms. Thus the concentration of excited atoms is some function of the concentration of ground state atoms and the observed kinetics would be

\[ \frac{\text{d}h\nu}{\text{d}t} = k_{41} \left[ \text{Cl}(^{2}\text{P}_{\frac{1}{2}}) \right] \left[ \text{Cl}(^{2}\text{P}_{\frac{3}{2}}) \right] \left[ \text{M} \right] = k_{41} k_{T} \left[ \text{Cl}(^{2}\text{P}_{\frac{3}{2}}) \right]^{2} \left[ \text{M} \right] \]

(42)

where \( k_{T} \) is the thermal distribution function between ground and excited atoms.

Intersystem crossing during the collision of two ground state Cl\( (^{2}\text{P}_{\frac{3}{2}}) \) atoms would, in all probability, require a third body. The third body (M) would be necessary either to induce the intersystem crossing or to stabilize the \( ^{3}\Pi_{0+} \) state after a spontaneous crossing.

In Douglas' paper, in the determination of the rotational constants of the \( ^{3}\Pi_{0+} \) state an anomalous behaviour in \( B \) can be seen at about the 12th or 13th vibrational level in the \( ^{3}\Pi_{0+} \) state. This same behaviour was also noted by Elliot in an earlier work at about the 10th vibrational level. Elliot's assignments were, however, in error by 2 vibrational levels and thus his results coincide with Douglas'. This anomaly could result from a perturbation on this level from mixing with another state which crosses at this point. Analysis of our spectrum would tend to support the intersystem crossing mechanism
in that much of the emission is originating from relatively high levels in the $^3\Pi_{0\nu}^+$ state. Moreover, no emission bands could be assigned to transitions occurring from vibrational levels greater than $v' = 13$, the perturbed level.

The problem could be resolved if accurate relative intensity measurements of various $v'$ series could be made. In this manner it may be possible to determine whether the emission results from an equilibrium vibrational distribution or is occurring preferentially from high vibrational levels near the postulated intersystem crossover.

The fourth order Cl atom dependence of the emission intensity reported by Uchida (24) was not observed. His deductions were based on calculated (degree of dissociation) atom concentrations and observable emission intensities at various high temperatures ($\approx 1000^\circ$K). He claimed that the emitting $^3\Pi_{0\nu}^+$ state could only be formed by a recombination process and that energy requirements negated excitation of ground state molecules to the excited state.

Calculations based on the assumption that this latter possibility is operative (for arbitrary but realistic transition energies) indicate that his observed intensities at the various temperatures can be adequately accounted for without recourse to his fourth order atom dependence. That
is, the emitting molecule need not be formed exclusively by a recombination process in his system.

The continuum observed by Palmer (25) and Uchida (24) was not observed in this work. They reported the continuum appearing only at high pressures (≈ 5 atmospheres) so it is quite unlikely that it would be observed in our system.
CONCLUSIONS AND SUGGESTIONS FOR FURTHER INVESTIGATION

The rate constants determined for the reaction

\[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \] (1)

in accord with the rate equation

\[ \frac{-d[\text{Cl}]}{dt} = 2k_{1\text{M}} [\text{Cl}]^2 [\text{M}] \] (1b)

where

\[ k_{1\text{Cl}_2} = 2.45 \times 10^{15} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \]

\[ k_{1\text{He}} = 0.3 \times 10^{16} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1} \]

Under the experimental conditions encountered (0.2 to 2.0 mm Hg) the gas phase decay was consistent with equation (1). No low pressure mechanism breakdown could be detected and we were unable to determine which of the three proposed mechanisms was operative.

The experimental method is well suited to the study of such atomic recombination reactions but certain refinements would increase the accuracy and range of the method.

The poison, while quite efficient, suffers from the possibility of minor variation in efficiency. Not only variation with time but local variations within the system. Some technique should be devised to ensure more uniformity in the effect of the poison. This may simply require more
frequent poisoning with a standardized procedure. The noted poison effect of acid surfaces \(^{(28)}\) suggests that the use of some more "acidic" glasses in the reaction system might remove the need for poisons completely.

The isothermal nature of the detector could be improved somewhat. This could be achieved by employing a thermally insulated support. This however suffers from the disadvantage that the detector readings would become a function of gas composition rather than energy content. Some system to ensure more rigid support of the detector coil without scraping the poisoned walls might be devised. This would not only ensure that the detector is in the same position with respect to the thermostated walls but may also eliminate some of the poison efficiency variations.

The spectroscopic study of the red glow accompanying the recombination proved it to be a band spectra attributable to a \( ^3\Pi_{0u}^+ \rightarrow \Sigma_g^+ \) transition. The decay of the emission was found to obey the relationship

\[
I = \frac{dh}{dt} = k_{41} [\text{Cl}]^2 [\text{M}]
\]

indicating that the \( ^5\Pi_{0u}^+ \) emitting state is formed in some recombination process similar to that for the gas phase recombination into the ground state. No decision
could be made as to whether the $^3\Pi_{0u}$ state was formed directly from the recombination of the appropriate atomic species (Cl$(^2P_{3/2}) +$ Cl$(^2P_{1/2})$) or formed by intersystem crossing during the recombination of two Cl$(^2P_{3/2})$ ground state atoms.

The experimental method used in determining the kinetic dependence of the emission does not give results as accurate as could be hoped for. Using a movable photomultiplier system to measure the emissive decay rather than the photographic method might give better results. Further studies should be conducted in which the relative intensity of the bands is measured accurately to establish the vibrational distribution in the upper state. This might provide information about the method of formation and the radiative lifetime of the upper $^3\Pi_{0u}$ state.
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