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KINETICS OF THE CHLORINE-ALKALINE PEROXIDE REACTION

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April 1990

Final Report

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Weapons Laboratory
Air Force Systems Command
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This technical report has been reviewed and is approved for publication.

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This report covers research into the kinetics of the liquid phase reaction between chlorine and basic hydrogen peroxide (BHP) to produce singlet delta oxygen. The accepted mechanism for this reaction is given in three steps. The second step involves only a proton transfer and is expected to be much faster than the other two steps. The focus of this research was to measure k_1 and k_3. Gas absorption measurements of chlorine in BHP in a laminar liquid jet absorber were carried out over the temperature range 1.8 to 8.9°C to determine k_1. The experimental data, obtained in the second-order kinetic regime, were interpreted using the penetration theory model. The k_1 measured is significantly lower than that estimated from previous work. Gas absorption measurements in a stirred cell absorber determined k_3. However, since this third step in the mechanism appears to have such fast kinetics, only a lower bound was determined for this rate constant. At 0°C, the data indicate that $k_3 > 500$ ℓ/s.)

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1.0 INTRODUCTION

The reaction between chlorine and basic hydrogen peroxide (BHP, a mixture of hydrogen peroxide, H_2O_2, and potassium hydroxide, KOH),

$$Cl_2 + H_2O_2 + 2KOH \longrightarrow 2KCl + 2H_2O + O_2(^1\Delta_g) \qquad (1)$$

is currently being utilized in several developmental programs to provide a source of singlet delta oxygen, $O_2(^1\Delta_g)$. The byproducts of the reaction in Equation 1 are potassium chloride (KCl) and water (H_2O). Typically an excess of hydrogen peroxide is used.

In the design and modeling of singlet oxygen generators, it is important to understand the kinetics of this reaction. A plausible mechanism for the reaction, as proposed by Hurst (Ref. 1), is given by

$$Cl_2 + HOO^- \xrightarrow{k_1} Cl^- + HOOCl \qquad (2)$$

$$HOOCl \xrightarrow{k_2} H^+ + ClOO^- \qquad (3)$$

$$ClOO^- \xrightarrow{k_3} O_2 + Cl^- \qquad (4)$$

The H^+ ion is then neutralized by

$$H^+ + HOO^- \longrightarrow H_2O_2 \qquad (5)$$

In reactions 2 to 4, k_1, k_2 and k_3 are the respective reaction rate constants. The reaction in Equation 3 (k_2) is very fast compared to the others, since it involves only a proton transfer. The rate-limiting step for the overall reaction appears to be Equation 2 (k_1). Thus, the rate of reaction of chlorine per unit volume of liquid in aqueous alkaline peroxide is given by $k_1[Cl_2][HOO^-]$, where k_1 is the second-order rate constant for the reaction given in Equation 2.

The purpose of this research is to measure the kinetic rate constants k_1 and k_3 for the reaction between chlorine and basic hydrogen peroxide and to correlate them using the Arrhenius expression. The approach taken to determine k_1 involves the measurement of the rate of absorption of chlorine into a flowing stream of BHP. A gas-liquid contacting device with a very small contact time between the gas and the liquid is required due to the estimated high value of k_1 (Refs. 2 to 5). The laminar liquid jet, with contact times between 10^{-3} and 10^{-2} s, is suitable for this purpose. Additional advantages possessed by the laminar liquid jet are that the gas-liquid contact area is well-defined and the hydrodynamics are well-known. The apparatus to determine k_3 is a modified stirred-cell absorber which can measure the rates of chlorine absorption and oxygen production.

2.0 DETERMINATION OF k_1

The reaction rate constant k_1 has been estimated to be of the order of 10^7 l/gmol·s in previous studies (Refs. 2 to 5). Sandall et al. (Ref. 6) studied the absorption of chlorine gas into a 6-molar aqueous sodium hydroxide solution in a roller drum reactor at 0 °C and at pressures lower than 0.27 kPa. They estimated the reaction rate coefficient to be 3×10^7 m^3/kg-mol·s. This is often used as an estimate for k_1 for the reaction of chlorine in aqueous BHP. Due to this expected high value of the rate constant, a gas-liquid contact device with a very small contact time is required. The laminar liquid jet, a gas-liquid contacting device with contact times in the range of 10^{-3} and 10^{-2} s, gives the lowest contact times of any of the common devices used for kinetic studies.

The laminar jet apparatus is shown in Figure 1. A jet of liquid enters the gas-space through a circular orifice 0.051 cm in diameter, and leaves through a receiver 0.1 cm in diameter. If the jet can be regarded as a cylindrical rod in uniform motion, the time of exposure to the gas of each element of its surface, t, is the length of the jet, h, divided by its velocity, $4L/\pi d^2$ (where L is the volumetric flow rate of liquid and d the diameter of the jet). Then

$$t = \frac{\pi d^2 h}{4L} \tag{6}$$

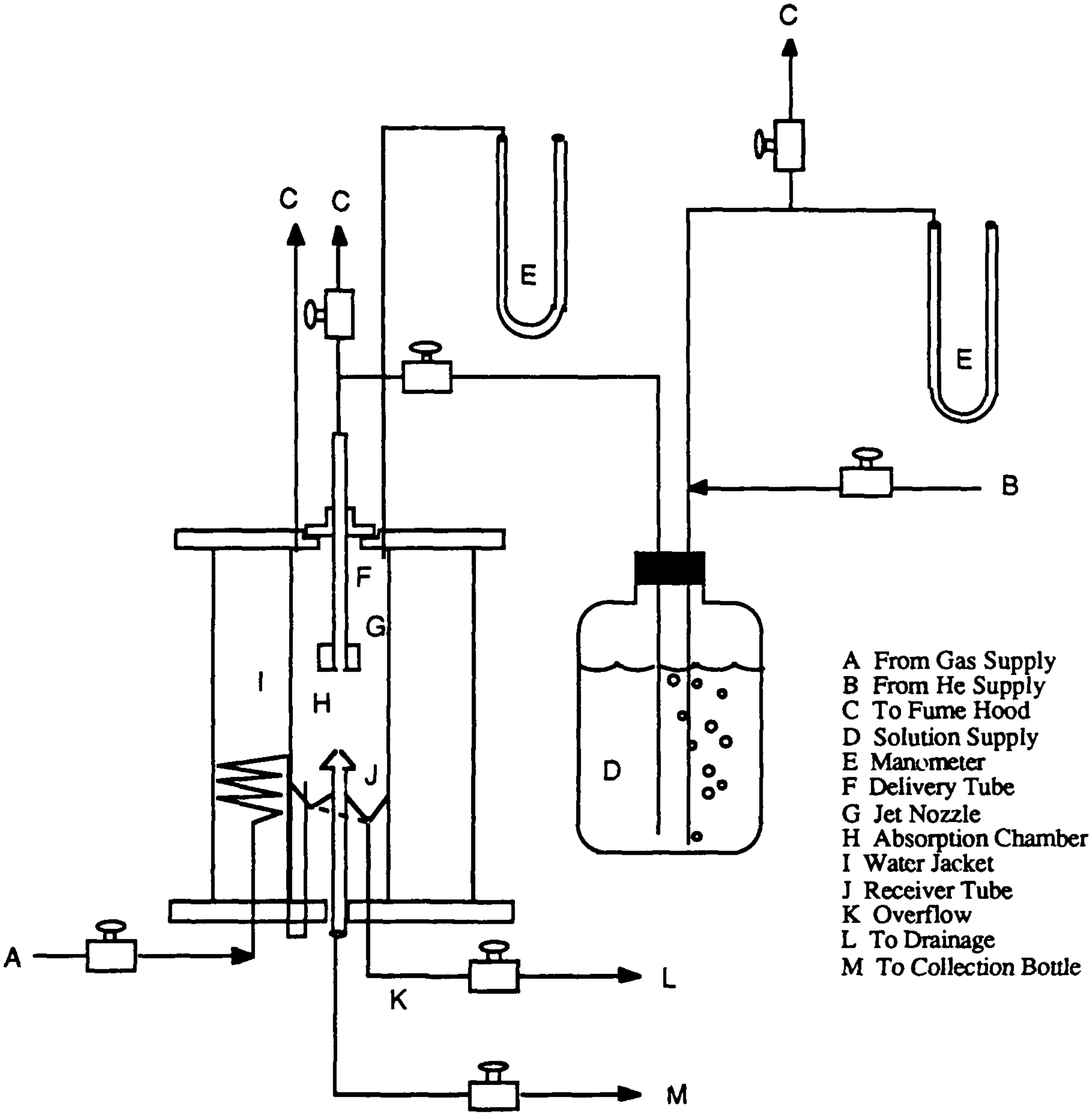
Thus, if one measures the rate of absorption of gas into the jet, q, one can calculate the amount Q absorbed by unit area of surface during a time of contact t

$$q = \frac{\pi d h Q}{t} \tag{7}$$

or

$$Q = \frac{qd}{4L} \tag{8}$$

The contact time can be varied by changing h and L, and thus Q can be determined as a function of contact time.



A From Gas Supply
B From He Supply
C To Fume Hood
D Solution Supply
E Manometer
F Delivery Tube
G Jet Nozzle
H Absorption Chamber
I Water Jacket
J Receiver Tube
K Overflow
L To Drainage
M To Collection Bottle

Figure 1. Laminar Liquid Jet Absorber.

According to the penetration theory (Ref. 7), when the gas is absorbed by the liquid without a chemical reaction (physical absorption), the amount of gas absorbed is given by

$$Q = 2\,A^{*}\sqrt{\frac{D_A t}{\pi}} \tag{9}$$

The rate of absorption for this case is

$$q = 4\,A^{*}\sqrt{D_A L h} \tag{10}$$

where A^{*} is the concentration of gas at the gas-liquid interface, and D_A is the diffusivity of the gas into the liquid.

For the case when the dissolved gas reacts with the liquid under fast first-order or pseudo-first-order reaction kinetics, the rate of absorption is given by

$$q = \pi A^{*} h\sqrt{D_A k_I} \tag{11}$$

This condition of pseudo-first-order kinetics occurs when the local rate of reaction depends only on the concentration of gas dissolved and the concentration of liquid reactant, B^{o}, can be regarded as constant. However, in order for a reaction to be considered as first-order or pseudo-first-order, the following condition has to be satisfied.

$$\sqrt{M} << E_i \tag{12}$$

Or, provided that

$$\sqrt{M} < \frac{1}{2}E_i \tag{13}$$

the rate of absorption follows the first-order equation within about 10%. M is the dimensionless rate constant given by

$$M = \frac{\pi}{4}k_{II}\,B^{o}t \tag{14}$$

and E_i is the instantaneous enhancement factor given by

$$E_i = 1 + \frac{B^{o}}{2A^{*}} \tag{15}$$

The pseudo-first-order rate constant, k_I, is related to the second-order rate constant, k_{II}, by $k_I = k_{II}B^o$. In order to satisfy the condition given by Equation 13 in our case, contact times of the order of 10^{-6} s would be required. This condition could also be met by having very low concentrations of chlorine at the BHP liquid interface.

When the dissolved gas undergoes a reaction with the liquid and the reaction rate depends on both the concentration of dissolved gas and the concentration of liquid (which cannot be regarded as constant) the kinetics are described by a second-order regime. For this case, the rate of gas absorption is given by

$$q = 4EA^* \sqrt{D_A Lh} \qquad (16)$$

where E is the enhancement factor for the gas absorption with reaction as compared with that for physical absorption. Under this regime the enhancement factor, E, can be determined by measuring the rate of gas absorption, q, at given values of the liquid flow rate and the height of the jet.

The enhancement factor for a second-order kinetics regime can be related to the dimensionless rate constant, M, by the empirical equation suggested by Brian et al. (Ref. 8).

$$E = \frac{\sqrt{M \frac{E_i - E}{E_i - 1}}}{\tanh \sqrt{M \frac{E_i - E}{E_i - 1}}} \qquad (17)$$

When the gas reacts instantaneously with a dissolved reactant, there is a plane beneath the surface where the concentration of both is zero and the rate of reaction is equal to the rate at which the two substances can diffuse to the reaction plane. The actual kinetics of the reaction are immaterial. For the case of instantaneous reaction, the rate of gas absorption is given by

$$q = 4E_iA^* \sqrt{D_A Lh} \qquad (18)$$

Thus, the approach to determine k_I is as follows:

- Measure the gas absorption rate of chlorine in BHP under instantaneous regime conditions to determine E_i by means of Equation 18.
- Measure the gas absorption rate of chlorine in BHP under second-order regime conditions to calculate the enhancement factor by using Equation 16.
- Calculate the value of the dimensionless rate constant M from Equation 17.
- Then k_I can be determined from M by using Equation 14.

In order for the reaction between chlorine and BHP to be in the second-order regime and as far as possible from the instantaneous regime, the concentration of reactant ($B^o = HOO^-$) needs to be high, yielding a high value of the instantaneous enhancement factor, E_i, according to Equation 15.

In order to determine k_1 in this manner, a knowledge of the chlorine solubility, A^*, and the chlorine diffusivity, D_A , are required to interpret the data. For the first part (the instantaneous regime experiments), these properties are required for a solution of aqueous hydrogen peroxide, since the concentration of reactant (HOO^-) is zero in the plane beneath the surface. For the second part (the second-order regime experiments), these properties are required for an aqueous BHP solution. In previous work (Ref. 9), these properties were measured experimentally in a 35% (wt) hydrogen peroxide aqueous solution, and the properties were estimated for BHP solutions. Due to the uncertainty of the estimates, and since the values of these properties are expected to be similar in both solutions, the experimental values of solubility and diffusivity of chlorine in 35% (wt) hydrogen peroxide have been used.

2.1 EXPERIMENTAL APPARATUS AND PROCEDURE

The laminar liquid jet shown in Figure 1 consists of an absorption chamber constructed from a 31-cm-long, 7.6-cm inside diameter (I.D.) Pyrex glass cylinder and is enclosed by a constant-temperature jacket constructed from a 31-cm-long, 16.5-cm-I.D. Pyrex glass cylinder. Both cylinders are held between two stainless steel flanges and the ends are sealed with Teflon gaskets. Ethylene glycol to the jacket is supplied from and recycled to a constant-temperature circulating bath.

The liquid feed is pumped to a surge tank, then through a rotameter and through a coil in the constant-temperature jacket. It is then fed to a 1-cm-I.D. delivery glass tube. The surge tank which is topped by a closed space of nitrogen gas helps in eliminating pump pulses. The delivery glass tube can slide in the vertical direction and can be locked in position by a swage-lock nut with Teflon ferrules. The gas supply is fed to a saturator, then through a coil in the constant-temperature jacket. It is then introduced into the absorption chamber at the base and is exhausted at the top of the chamber. The exhaust line is connected backward to a soap film meter, so that, when the gas inlet is closed, the gas retrieved to the chamber from the absorption will flow forward through the soap film meter.

The jet nozzle assembly is fitted onto the end of the glass delivery tube by three O-rings. The jet nozzle is a square-edged orifice, 0.051 cm in diameter, drilled in 0.008-cm-thick stainless steel. This nozzle design was recommended by Raimondi and Toor (Ref. 10) for absorption rate results closest to the theoretical values for rod-like flow and no interfacial resistance. The receiver is 1-cm-I.D. glass tube fitted into a funnel-shaped base, and is capped by a Teflon plug in which a 0.1-cm hole is drilled. A hole in the base allows draining of any liquid overflow. The jet is centered by manipulating the mount of the delivery tube relative to the top flange. The jet is considered centered when all of its contents empty into the receiver with no overflow.

A leveling device consisting of a cup with an overflow drain is used to precisely adjust the liquid level in the receiver tube. If the level is low, gas entrainment occurs; if high, then the liquid overflows. The liquid level has to be readjusted after any changes in the liquid flow rate. The length of the jet is measured by a cathetometer with an error less than 0.5×10^{-2} cm.

The temperature of the system is monitored by thermometers in the constant-temperature jacket, in the jet chamber, and in the liquid delivery tube. The temperatures are controlled to within ± 0.30 °C.

After the jet is flowing satisfactorily, the gas is turned on long enough for the jet chamber and all the tubings to fill with the gas. Then the gas is turned off; the rate of gas absorption is found by measuring the amount of time needed for a soap film to travel through a certain volume.

The BHP was prepared from 90% (wt) hydrogen peroxide and 6-molar potassium hydroxide (KOH) solutions. Typical BHP solutions are prepared by mixing equal volumes of these two solutions which yields a concentration of HOO^- of about 3 molar. Higher concentrations are desired, but the decomposition rate of the BHP solution increases with the concentration of HOO^- to a point at which it can be very dangerous. The highest concentration that could be handled safely in the laminar jet apparatus was about 4 molar in HOO^-. The calculated amount of 90% (wt) H_2O_2 was poured into a Pyrex bottle and surrounded by liquid cooled with dry ice to lower the temperature to about -20 °C. Then the right amount of 6-molar KOH solution was mixed dropwise, while the solution was stirred and the temperature controlled to avoid uncontrolled decomposition. This solution was kept at that low temperature until it was fed to the jet. The 6-molar KOH solution was prepared from KOH pellets and deionized and distilled water. After the KOH solution was prepared, activated carbon was added to remove any impurities from the KOH pellets. This procedure reduced the rate of decomposition of the BHP solution.

Experimental difficulties were found with the system chlorine-BHP in the laminar jet and many modifications to the apparatus were made. High rates of decomposition of the BHP were noticed when the solution was fed from the bottle to the jet through the pump; therefore, a different device was used to transfer the BHP solution to the jet. The bottle containing the BHP solution was kept at the temperature of the experiment by cooling it with a circulator bath and the liquid was transferred to the jet by pressurizing the bottle with nitrogen. The pressure above the liquid was controlled by a gas regulator which allowed control of the liquid flow rate. Thus, the surge tank, the coil in the constant-temperature jacket and the rotameter were eliminated. The liquid flow rate was measured, after obtaining steady conditions, by measuring the volume of liquid collected at the exit in a given period of time.

To adjust the liquid level in the receiver tank, a valve was used instead of the cup. Although it improved the conditions, the level inside the receiver was very difficult to control. Gas bubbles were released from the receiver tube, due to the decomposition of BHP, making it impossible to have a well-defined gas-liquid interface at the tip of the receiver. Instead, the bubbles from the decomposition formed foam at the top of the receiver.

The rate of gas absorption was determined by measuring the concentration of Cl^- in the solution after absorption instead of using a bubble meter. Samples were taken at the exit and neutralized with 2-molar HNO_3, and ionic strength adjustor was used according to the procedure described by Kumar and McCluskey (Ref. 3); then the solution was put in contact with a chloride ion selective electrode to measure the chloride concentration, $[Cl^-]$. The rate of gas absorption was calculated as $q = L[Cl^-]/2$.

2.2 EXPERIMENTAL RESULTS

The laminar liquid jet was adjusted to yield the highest contact time by using low liquid flow rates, L, and large heights, h, without the appearance of turbulence at the end of the jet in order to carry out gas absorption in the instantaneous regime. The gas absorption rate of chlorine, q, was measured and the instantaneous enhancement factor, E_i, was calculated using Equation 18. The results are shown in Table 1 and Figure 2 for a height of the liquid jet of $h = 2.77$ cm. The enhancement factor was measured at the same conditions with slightly lower contact time and no appreciable change was noticed (within experimental error), indicating that the regime was instantaneous.

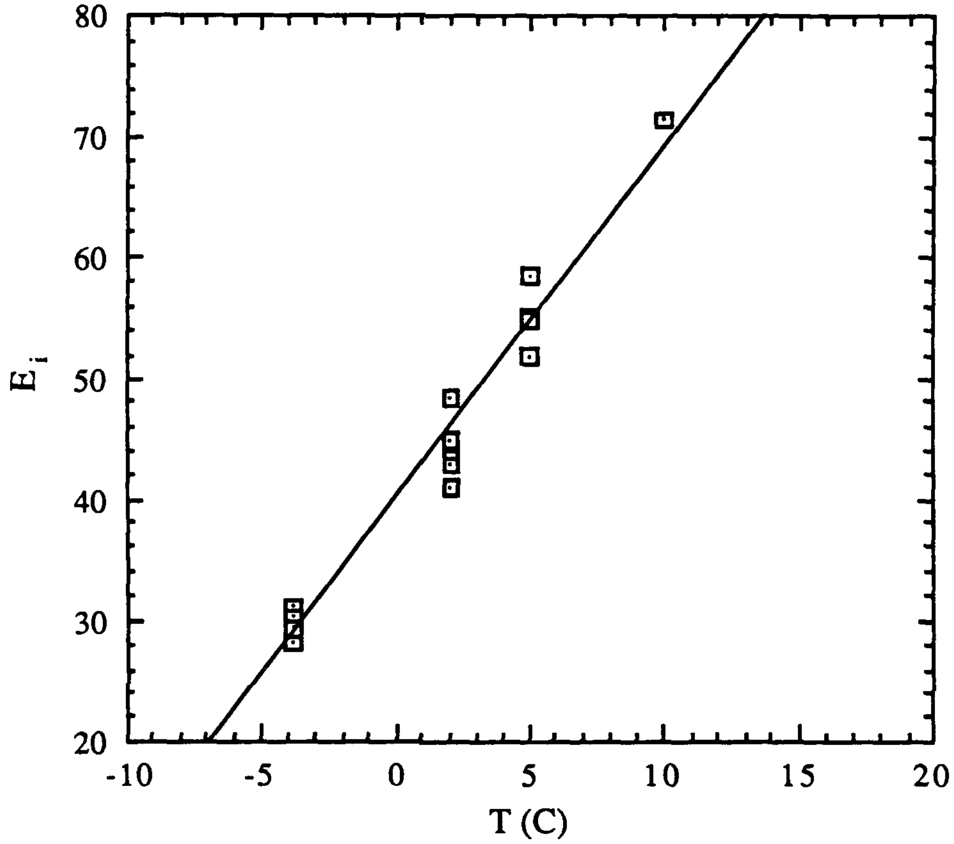


Figure 2. Experimental results for the instantaneous enhancement factor as a function of temperature for chlorine in basic hydrogen peroxide solution (4 M).

The results in Table 1 are correlated by

$$E_i = 40.128 + 2.8957\ T(^\circ C) \tag{19}$$

which is the equation for the line in Figure 2.

TABLE 1. Experimental results for the instantaneous enhancement factor.

T (°C)	T (K)	L (cm^3/s)	q x 10^5 (gmol/s)	E_i
-3.9	269.25	0.683	5.79	28.21
-3.9	269.25	0.683	6.40	31.19
-3.9	269.25	0.683	6.10	29.72
-3.9	269.25	0.683	6.20	30.21
-3.9	269.25	0.683	6.02	29.33
2.0	275.15	0.633	6.75	44.11
2.0	275.15	0.633	6.83	44.64
2.0	275.15	0.633	6.87	44.90
2.0	275.15	0.633	7.42	48.49
2.0	275.15	0.633	6.29	41.11
2.0	275.15	0.633	6.57	42.94
5.0	278.15	0.600	7.69	58.70
5.0	278.15	0.600	7.23	55.18
5.0	278.15	0.600	7.21	55.03
5.0	278.15	0.600	7.17	54.73
5.0	278.15	0.600	6.79	51.83
10.0	283.15	0.733	8.38	71.48

For the second-order regime experiments, the laminar liquid jet was adjusted to yield considerably lower contact times than that in the instantaneous regime. Again, the gas absorption rate of chlorine, q, was measured and the enhancement factor, E, was calculated using Equation 16. The results are shown in Table 2 and Figure 3 for a height of the liquid jet of h = 1.23 cm. The

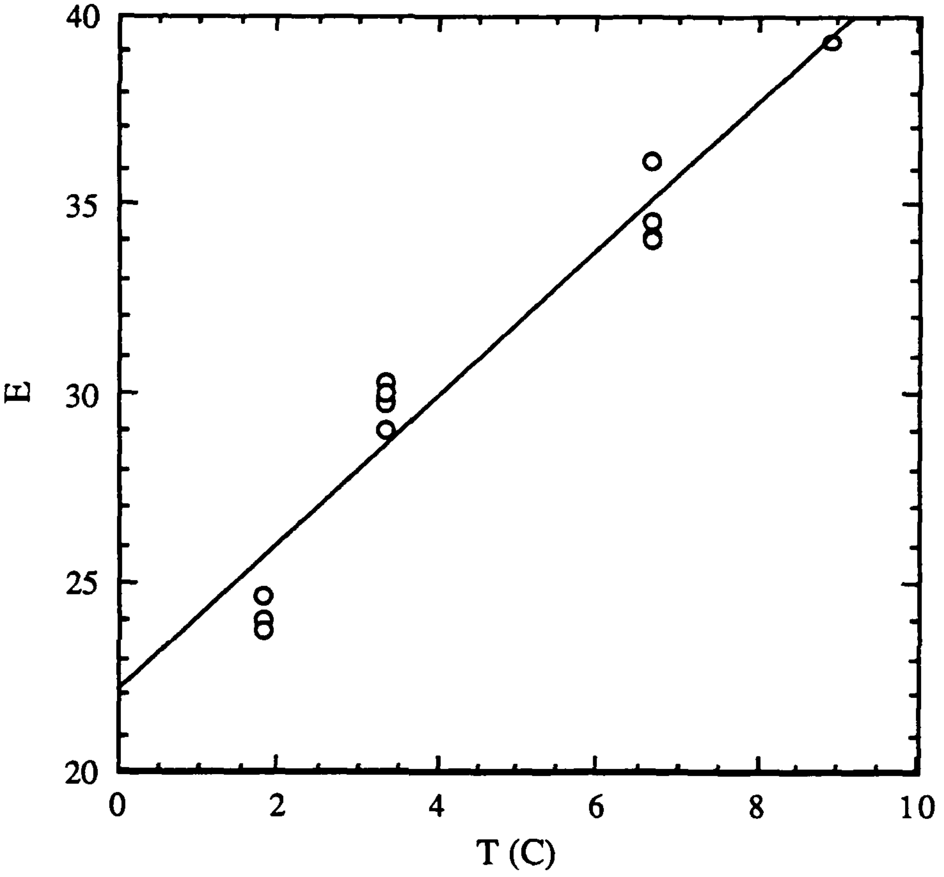


Figure 3. Experimental results for the enhancement factor as a function of temperature for chlorine in basic hydrogen peroxide solution (4 M).

difference between this enhancement factor and the instantaneous enhancement factor (measured at the same temperature and HOO^- concentration) was used as a proof of the second-order regime conditions.

The dimensionless rate constant, M, and the second-order rate constant, k_1, were calculated from these values using Equations 17 and 14, respectively, and the results are shown in Table 3.

The values obtained for the second-order rate constant were correlated as a function of temperature by the Arrhenius equation as

$$\ln k_1 = 47.92 - \frac{9872.0}{T(K)} \qquad (20a)$$

or in the Arrhenius form

$$k_1 \text{ (l/gmol s)} = 6.4773 \times 10^{20} \exp\left(- \frac{9872.0}{T(K)}\right) \qquad (20b)$$

These results are also shown in Figure 4 in which the line is given by Equation 20.

TABLE 2. Experimental results for the second-order enhancement factor.

T (°C)	T (K)	L (cm^3/s)	q x 10^5 (gmol/s)	E
1.8	274.95	0.950	3.03	24.05
1.8	274.95	0.950	2.99	23.73
1.8	274.95	0.950	3.10	24.60
3.3	276.45	0.917	3.37	29.04
3.3	276.45	0.917	3.52	30.33
3.3	276.45	0.917	3.46	29.81
3.3	276.45	0.917	3.45	29.73
3.3	276.45	0.867	3.39	30.04
6.7	279.85	0.883	3.36	34.10
6.7	279.85	0.883	3.56	36.13
6.7	279.85	0.883	3.35	34.00
6.7	279.85	0.883	3.40	34.51
8.9	282.05	0.883	3.53	39.31

TABLE 3. Experimental results for the second-order rate constant k_1.

T (°C)	T (K)	t x 10^3 (s)	E_i	E	M	k_1 x 10^{-5} (l/gmol·s)
1.8	274.95	2.856	45.34	24.05	1204.61	1.342
1.8	274.95	2.856	45.34	23.73	1155.40	1.288
1.8	274.95	2.856	45.34	24.60	1293.76	1.442
3.3	276.45	2.960	49.68	29.04	1988.79	2.139
3.3	276.45	2.960	49.68	30.33	2314.00	2.488
3.3	276.45	2.960	49.68	29.81	2176.84	2.341
3.3	276.45	2.960	49.68	29.73	2156.50	2.319
3.3	276.45	2.856	49.68	30.04	2236.45	2.492
6.7	279.85	3.073	59.53	34.10	2676.39	2.772
6.7	279.85	3.073	59.53	36.13	3265.18	3.382
6.7	279.85	3.073	59.53	34.00	2650.29	2.745
6.7	279.85	3.073	59.53	34.51	2786.05	2.886
8.9	282.05	3.073	65.90	39.31	3771.68	3.907

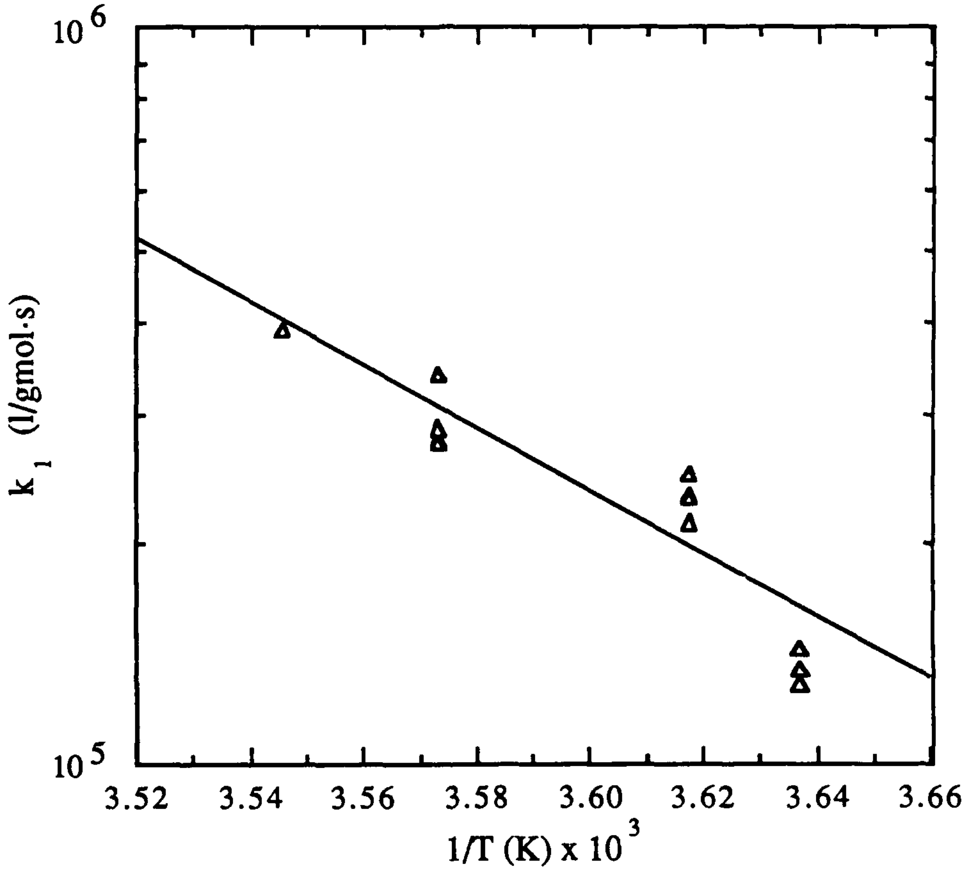


Figure 4. Rate constant for the reaction between chlorine and peroxyl ion as a function of temperature.

3.0 DETERMINATION OF k_3

An experiment was performed to determine the reaction rate constant, k_3, for the following reaction sequence

$$Cl_2 + HOO^- \xrightarrow{k_1} Cl^- + HOOCl \qquad (21)$$

$$HOOCl \xrightarrow{k_2} H^+ + ClOO^- \qquad (22)$$

$$ClOO^- \xrightarrow{k_3} O_2 + Cl^- \qquad (23)$$

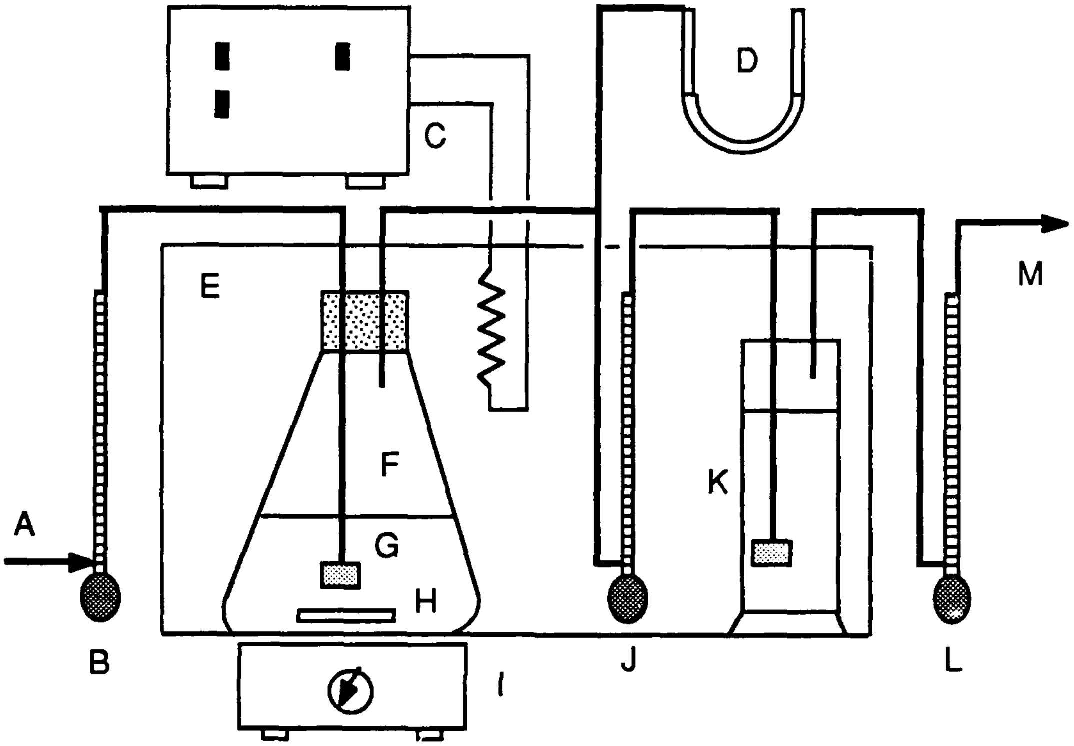
The reaction rate of the third reaction is assumed to be first order with respect to the chlorite ion concentration

$$r_{ClOO^-} = k_3[ClOO^-] \qquad (24)$$

3.1 EXPERIMENTAL APPARATUS AND PROCEDURE

A small stirred cell shown in Figure 5 was used to facilitate the reaction of Cl_2 with BHP. The reactor operated in semi-batch mode. The Cl_2 gas was mixed into the liquid BHP from a gas dispersion tube. The liquid was mixed with a magnetic stirrer so that there would be no liquid phase mass transfer resistance. The rates of gas entering and leaving the reactor were measured with a soap film bubble meter. The bubble meters have a capacity of 100 ml and the gas flow rates were timed with a stopwatch. The unreacted Cl_2 was stripped from the exit gas stream by contacting with concentrated sodium hydroxide. Finally, the O_2 production rate was measured with a bubble meter. The apparatus was immersed in a circulating bath to maintain a constant temperature of 0 °C. The pressure was maintained near atmospheric conditions.

A 4-M BHP solution was prepared with distilled water, 90% (wt) H_2O_2 and an aqueous solution saturated with KOH. The KOH solution was initially mixed with activated carbon and filtered to remove any remaining impurities that might have enhanced decomposition.



A	Cl_2 GAS INLET STREAM	H	MAGNETIC STIRRING BAR
B	Cl_2 BUBBLE METER	I	MAGNETIC STIRRER
C	CIRCULATING BATH	J	Cl_2/O_2 BUBBLE METER
D	MANOMETER	K	Cl_2 STRIPPER
E	BATH	L	O_2 BUBBLE METER
F	REACTOR	M	O_2 GAS EXIT STREAM
G	GAS DISPERSION TUBE		

Figure 5. Stirred Cell for Cl_2 gas absorption and O_2 desorption measurements.

Initially, the reaction chamber was charged with the BHP solution, and the air above the liquid in the system was evacuated under approximately 1 atm of vacuum. When the Cl_2 gas was released to the system, the vacuum was immediately filled with Cl_2 gas and the system was then opened to the atmosphere. The three gas flow rates were measured initially and then every minute. There was a 20-s lag between the measurements of each gas stream.

The data appear in Table 4. The data from Runs 1 and 8 are plotted in Figure 6. There was a limitation on the maximum gas flow rate measurable with the bubble meters. At higher flow rates than those reported here, the soap film would break. The accuracy of the measurements also decreased at higher gas flow rates, as is evident in the comparison between the flow rates of Runs 1 and 8 in Figure 6.

The results indicate that, within experimental error, all of the Cl_2 gas fed to the reactor was chemically absorbed into the liquid BHP, and that the O_2 production rate was equal to the rate of absorption of Cl_2. This is explained if the reaction in Equation 21 is the rate-limiting step. Therefore,

$$r_{ClOO^-} = r_{Cl_2} \tag{25}$$

and

$$r_{Cl_2} = -r_{O_2} \tag{26}$$

In the apparatus described here, the production of O_2 was limited only by the rate at which Cl_2 is fed to the reactor. Under the observed conditions, only a lower bound can be determined on the rate constant k_3.

3.2 ANALYSIS OF RESULTS

In order to estimate the lower bound on the reaction rate constant k_3, the experimental results are used to get a lower bound on the quantity

$$\frac{r_{ClOO^-}}{[ClOO^-]} = k_3 \tag{27}$$

Where r_{ClOO^-} is the rate of reaction of $ClOO^-$ and is equal to the rate of production of O_2,

$$r_{ClOO^-} = -r_{O_2} \tag{28}$$

Table 4. Experimental data for reaction of Cl_2 with 4-M BHP at 0°C.

Run #	Cl_2 $\left(\frac{gmol}{s}\right) \times 10^4$	Cl_2+O_2 $\left(\frac{gmol}{s}\right) \times 10^4$	O_2 $\left(\frac{gmol}{s}\right) \times 10^4$
1	3.32	3.36	3.39
	3.29	3.35	3.37
	3.32	3.31	3.35
	3.40	3.36	3.34
	3.32	3.40	3.31
	3.31	3.32	3.32
	3.33	3.35	3.34
2	3.27	3.30	3.33
	3.35	3.28	3.34
	3.25	3.25	3.32
	3.30	3.34	3.29
	3.32	3.29	3.30
	3.32	3.24	3.27
	3.18	3.29	3.28
	3.26	3.23	3.33
3	3.36	3.31	3.33
	3.36	3.41	3.30
	3.40	3.33	3.36
	3.40	3.31	3.27
	3.43	3.38	3.38
	3.38	3.32	3.43
	3.35	3.43	3.36
4	3.29	3.39	3.45
	3.33	3.44	3.36
	3.40	3.38	3.30
	3.43	3.52	3.57
	3.41	3.46	3.45
	3.40	3.32	3.33
5	3.43	3.42	3.36
	3.37	3.42	3.47
	3.39	3.43	3.50
	3.44	3.40	3.45
	3.32	3.41	3.43
	3.43	3.42	3.39
	3.35	3.46	3.48
6	3.40	3.52	3.53
	3.44	3.45	3.44
	3.42	3.40	3.58
	3.42	3.54	3.53
	3.49	3.48	3.51
	3.33	3.48	3.54
7	3.53	3.50	3.44
	3.45	3.59	3.51
	3.43	3.47	3.46
	3.45	3.55	3.62
	3.57	3.60	3.58
	3.40	3.45	3.50
8	3.68	3.68	3.71
	3.65	3.64	3.63
	3.73	3.58	3.61
	3.59	3.67	3.65
	3.84	3.68	3.69

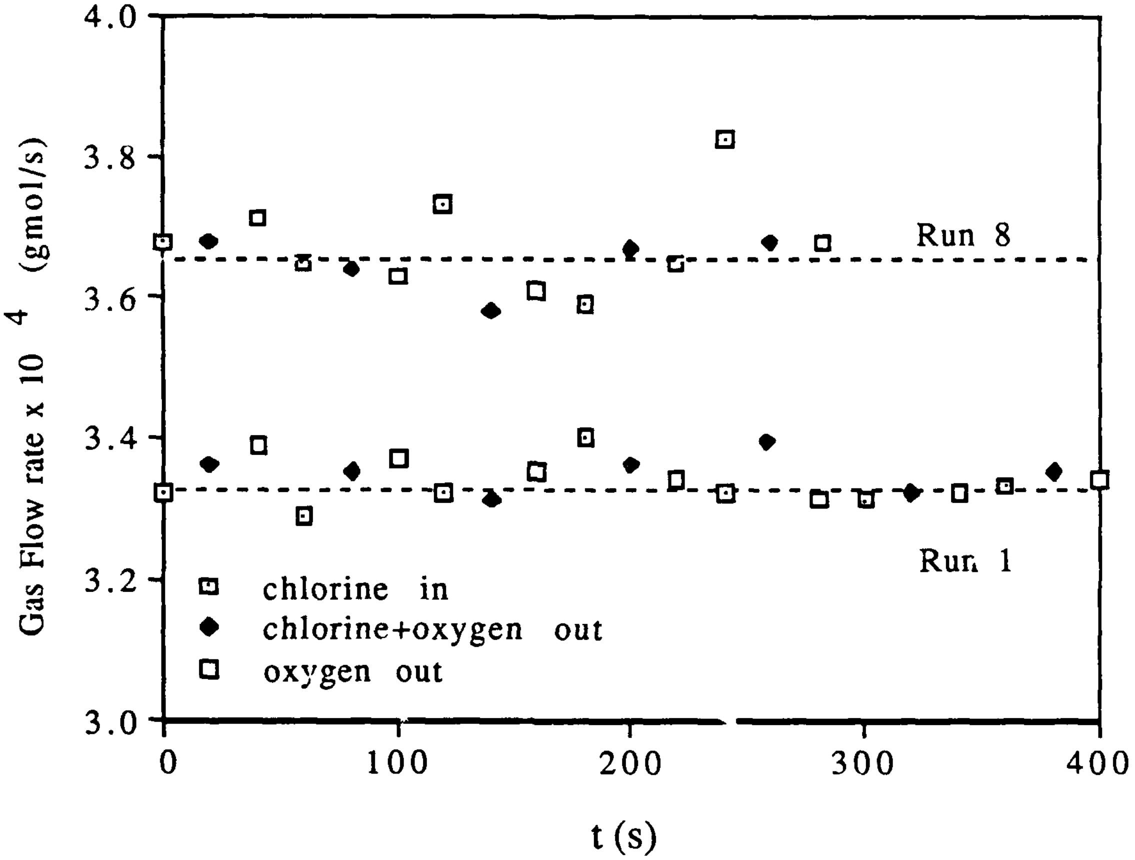


Figure 6. Molar flow rate vs. time for Runs 1 and 8 from the data in Table 4.

The chlorite ion concentration can be determined from species mass balances around the reacting system.

Let A = moles Cl_2 absorbed due to reaction 21

B = moles O_2 produced from reaction 23

C = moles Cl^- in solution from reactions 21 and 23

D = moles $ClOO^-$ in solution

The relationships are

$$A = \frac{C + D}{2} \tag{29}$$

$$C = A + B \tag{30}$$

Equations 29 and 30 can be solved for the unknown D in terms of the measurable quantities, A and B.

$$D = A - B \tag{31}$$

The experimental result for the chlorite ion concentration is

$$D = 0 \pm e(A) \pm e(B) \tag{32}$$

where e(A) and e(B) are the experimental errors associated with the values of A and B. The error, e(A) or e(B) is calculated as

$$e(i) = G_i\, p\, t' \tag{33}$$

where

G_i = the initial gas flow rate (gmol/s)
p = the relative precision of the bubble meter (± 0.1 ml/100 ml = ± 0.001)
t' = the estimated minimum time elapsed before the initial reading (≈ 1 s)

Note that the result of Equation 33 is e(A) = e(B). Combining Equations 30, 32 and 33 with Equations 25 and 26 gives

$$k_3 > \frac{1}{2pt'} \tag{34}$$

The lower bound on k_3 from Equation 34 is

$$k_3 > 500 \text{ s}^{-1} \text{ at } 0\ ^\circ\text{C} \tag{35}$$

The main source of limitations in the experiment outlined here was the bubble meter measurement of the gas flow rates. Although the precision of the bubble meter was good, the reactions proceeded very fast. The time scale of the reaction rate was very small relative to the time scale of the gas flow rate measurement with the bubble meter. The estimate of the lower bound on k_3 was limited by t, the time elapsed before the initial gas flow rate measurement.

REFERENCES

1 Held, A. M., Halko, D. J., and Hurst, J. K., "Mechanisms of Chlorine Oxidation of Hydrogen Peroxide", J. Am. Chem. Soc., **100**, 5732 (1978).

2 Zagidullin, M. V., Igoshin, V. I., Katulin, V. A., and Kupriyanov, N. L., "Possibility of using an atomizer in a chemical generator of singlet oxygen for an oxygen-iodine laser", Sov. J. Quantum Electron., **13**, 494 (1983).

3 Kumar, A. and McCluskey, R. J., "Study of the Chlorine-Alkaline Hydrogen Peroxide Reaction", Ind. Eng. Chem. Res. (ACS), **26**, 1323-1329 (1987).

4 Richardson, R. J., Kelley, J. D., and Wiswall, C. E., "Singlet oxygen generation mechanisms in the chemically pumped iodine laser", J. Appl. Phys., **52**, 1066 (1981).

5 Richardson, R. J., Wiswall, C. E., Carr, P. A. G., Hovis, F. E., and Lilenfeld, H. V., "An efficient singlet oxygen generator for chemically pumped iodine lasers", J. Appl. Phys., **52**, 4962 (1981).

6 Sandall, O. C., Goldberg, I. B., Hurlock, S. C., Laeger, H. O., and Wagner, R. I., "Solubility and rate of hydrolysis of chlorine in aqueous sodium hydroxide at 273 K", AIChE J., **27**, 856-859 (1981).

7 Danckwerts, P. V., "Gas-Liquid Reactions", McGraw-Hill Book Co., New York, N. Y., 1970.

8 Brian, P. L. T., Hurley, J. F., and Hasseltine, E. H., "Penetration Theory for Gas Absorption Accompanied by a Second Order Chemical Reaction", AIChE J., **7**, 226-231 (1961).

9 Sandall, O. C., Ruiz-Ibanez, G., Bidarian, A., and Davis, R., Measurement and correlation of the solubility and diffusion coefficient for oxygen and chlorine in basic hydrogen peroxide, AFWL-TR-89-14, Air Force Weapons Laboratory, Kirtland AFB, N. Mex., Aug 1989.

10 Raimondi, P. and Toor, H. L., "Absorption of CO_2 in water in a Laminar Liquid Jet", AIChE J., **5**, 86 (1959).

ABBREVIATIONS, ACRONYMS AND SYMBOLS

A	Moles Cl_2 absorbed due to reaction 21
A^*	Concentration of the gas at the interface gas-liquid (gmol/cm^3)
B	Moles of oxygen produced from reaction 23
B^o	Concentration of reactant in solution (gmol/cm^3)
BHP	Basic hydrogen peroxide
C	Moles of chloride ion in solution from reactions 21 and 23
Cl_2	Chlorine
Cl^-	Chloride ion
$ClOO^-$	Chlorite ion
D	Moles of chlorite ion in solution
D_A	Diffusion coefficient of gas in liquid (cm^2/s)
d	Diameter of the liquid laminar jet (d = 0.051 cm)
E	Enhancement factor
E_i	Instantaneous enhancement factor
e	Experimental error
G_i	Initial gas flow rate (gmol/s)
h	Length of the liquid laminar jet (cm)
H^+	Hydrogen ion
H_2O	Water
H_2O_2	Hydrogen Peroxide
HOO^-	Peroxyl ion
HOOCl	Chlorous acid

KCl	Potassium Chloride
KOH	Potassium Hydroxide
k_I	First or pseudo-first-order rate constant (1/s)
k_{II}	Second-order rate constant (l/gmol s)
k_1	Rate constant for the reaction in Equation 2
k_2	Rate constant for the reaction in Equation 3
k_3	Rate constant for the reaction in Equation 4
L	Liquid flow rate (cm^3/s)
M	Dimensionless rate constant defined by Equation 14
O_2	Oxygen
$O_2(^1\Delta_g)$	Singlet Delta Oxygen
p	Relative precision of the bubble meter
Q	Total gas absorption ($gmol/cm^2$)
q	Gas absorption rate (gmol/s)
r_{Cl_2}	Rate of chlorine consumption
r_{ClOO^-}	Rate of reaction in Equation 23
r_{O_2}	Rate of oxygen production
T	Temperature (K)
t	Contact time defined by Equation 6 (s)
t'	The estimated minimum time elapsed before the initial reading (≈ 1 s)

Greek Symbol

π	Constant = 3.14159