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STUDY OF THE CHLORINE-BASIC HYDROGEN PEROXIDE REACTION  
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R J MCCLUSKEY 1982 AFOSR-TR-83-0430 AFOSR-81-0155

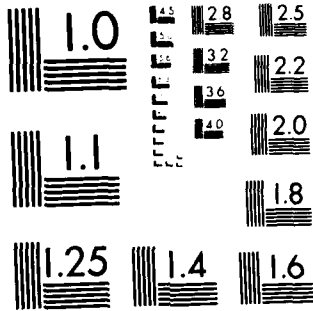
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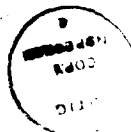
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The reaction of chlorine with alkaline hydrogen peroxide solutions, approximately 2.5M in O<sub>2</sub>H<sup>-</sup>, has been examined in an unagitated batch reactor at 10 degrees C. Initial chlorine partial pressures of up to 450 torr and reaction times of one, three and six minutes were investigated. The results are in qualitative agreement with the theory for absorption with an instantaneous reaction, in which the rate of reaction becomes controlled by liquid phase mass transfer after an initial, rapid reaction depletes the interfacial region of O<sub>2</sub>H<sup>-</sup> reactant. The effective anion diffusivity was on the order of 7 times 10<sup>(-4)</sup> sq. cm per sec, a value much larger than typical liquid diffusivities. The rate of reaction declined faster than the time (-1/2) dependence predicted by the theory for absorption with an instantaneous reaction. In one minute's time, complete conversion of all added chlorine to chloride ion was achieved until 4.7 times 10<sup>(-4)</sup> moles of chlorine per sq. cm of interfacial area had reacted. Subsequent reaction was almost independent of initial chlorine partial pressure. The amount of chlorine reaction was not sensitive to the rate of oxygen produced by hydrogen peroxide disproportionation. The rate of disproportionation was seen to depend in a complicated manner on the composition of the alkaline solutions.

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AFOSR-TR- 83 - 0430

FINAL REPORT

AFOSR-81-0155

CLARKSON COLLEGE OF TECHNOLOGY

Richard J. McCluskey

Study of the Chlorine-Basic Hydrogen Peroxide Reaction

## Abstract

The reaction of chlorine with alkaline hydrogen peroxide solutions, approximately 2.5M in  $O_2H^-$ , has been examined in an unagitated batch reactor at  $10^\circ C$ . Initial chlorine partial pressures of up to 450 torr and reaction times of one, three and six minutes were investigated. The results are qualitatively in agreement with the theory for absorption with an instantaneous reaction, in which the rate of reaction becomes controlled by liquid phase mass transfer after an initial, rapid reaction depletes the interfacial region of  $O_2H^-$  reactant.

The effective anion diffusivity was on the order of  $7 \times 10^{-4} \text{ cm}^2/\text{s}$ , a value much larger than typical liquid diffusivities. Also, the rate of reaction declined faster than the  $\text{time}^{-1/2}$  dependence predicted by the theory for absorption with an instantaneous reaction.

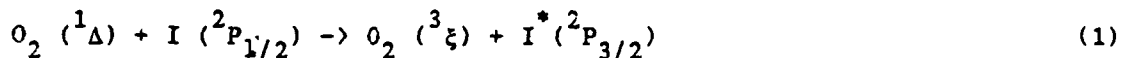
In one minute's time, complete conversion of all added chlorine to chloride ion was achieved until  $4.7 \times 10^{-4}$  moles of chlorine per  $\text{cm}^2$  of interfacial area had reacted. Subsequent reaction was almost independent of initial chlorine partial pressure.

The amount of chlorine reaction was not sensitive to the rate of oxygen produced by hydrogen peroxide disproportionation. The rate of disproportionation was seen to depend in a complicated manner on the composition of the alkaline solutions.

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## Introduction

It has been demonstrated that an oxygen-iodine chemical laser can be operated using mixtures of molecular iodine and molecular oxygen in its first electronic excited state,  $^1\Delta$  [1]. Lasing occurs on the  $^2P_{1/2} \rightarrow ^2P_{3/2}$  spin orbit transition of atomic iodine, which is pumped by the reaction:

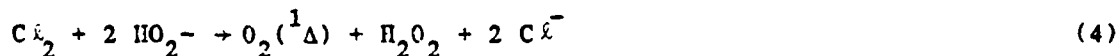


A population inversion will result if the excited oxygen constitutes greater than 17% of the total oxygen [2].

High gas phase concentrations of  $O_2 (^1\Delta)$  have been achieved in the laboratory by bubbling chlorine gas through alkaline hydrogen peroxide solutions. The mechanism of singlet delta oxygen generation is believed to be:

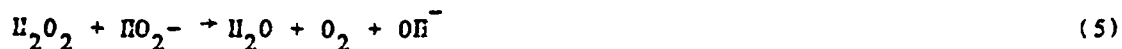


These two steps give a net reaction of:



This reaction must take place at or very near the gas-liquid interface since high yields of  $O_2 (^1\Delta)$  are obtained despite it having a lifetime of only a few microseconds in aqueous solutions [3].

Details of the process by which singlet delta oxygen is produced are poorly understood. This reaction system is complicated by a number of factors: the rapidity of the reaction, a gas phase resistance to the reaction, the disproportionation reaction



that always occurs in alkaline hydrogen peroxide solutions, and the relatively high exothermicity of reactions (4) and (5).

It is desirable to design reactors that can rapidly produce high gas phase concentrations of  $\text{O}_2(^1\Delta)$  in an efficient manner. An important measure of efficiency for a portable chemical laser is the amount of  $\text{O}_2(^1\Delta)$  produced per unit weight of reactants.

This report describes a series of experiments carried out to investigate the maximum amount of  $\text{O}_2(^1\Delta)$  production, via reaction (4), that can take place at a reasonably stationary gas-liquid interface. This involved the batchwise reaction of gaseous chlorine, at partial pressures of up to 450 torr, with alkaline hydrogen peroxide solutions approximately 3M in KOH. The extent of reaction was monitored by measuring the chloride ion concentration with an ion specific electrode.

#### Literature Review

The rate of reaction (4) is very fast, a fact consistent with the idea that it occurs at or very close to the liquid-gas interface. An approximate measurement of the liquid phase reaction rate constant has not been made. However, the very similar reaction of chlorine with sodium hydroxide solution,



has been relatively well studied. No gaseous product is involved in this reaction system, so all diffusional resistance to reaction may be considered as lying in the liquid phase. H. Hikita et al. [4] used a liquid jet reaction apparatus to measure the chlorine absorption rate with chemical



reaction at atmospheric pressure, 30°C and base concentration at 0.05 to 0.30 M. H. Takahashi et. al. [5] had performed similar experiments with a stop-cock absorber at the same temperature, pressure and base concentrations. The results of both groups show the absorption flux varied as the exposure time to the -1/2 power. This functional dependence, which held over a 5-order range of exposure times, is the theoretically predicted relationship for absorption with instantaneous reaction [6]. O. Sandall et. al. [7] studied the same reaction system using a roller-drum reactor at 0°C, pressures below 2 torr, and a base concentration of 6 M. They obtained an estimate of the pseudo-first order rate constant of  $3 \times 10^7$  l/g-mol-s. Measurement of the reaction rate of chlorine with alkaline hydrogen peroxide solution was attempted by McCluskey using a liquid jet apparatus similar to Nikita's but working at pressures below 30 torr [8]. Under steady state conditions, the gaseous chlorine must diffuse through a mixture of oxygen and water vapor to reach the liquid interface. There is therefore a gas phase diffusional resistance to reaction. The simplest way to account for this is through a gas phase mass transfer coefficient defined by equation (7)

$$N_{Cl_2} = k_G (P_{Cl_2} - P_{Cl_2}^*) \quad (7)$$

where  $N_{Cl_2}$  = steady state flux of  $Cl_2$

$P_{Cl_2}$  = partial pressure of chlorine in the bulk gas

$P_{Cl_2}^*$  = partial pressure of chlorine at the interface

Assuming vapor-liquid equilibrium occurs at the interface allows the steady state chlorine flux to be expressed as:

$$N_{Cl_2} = \left( \frac{1}{\frac{1}{k_G} + \frac{1}{H \sqrt{Dk} C_{HO_2^-}}} \right) P_{Cl_2} \quad (8)$$

where H = Henry's law constant

D = liquid phase diffusivity of chlorine

k = liquid phase pseudo-first order reaction rate constant

$C_{HO_2^-}$  = liquid phase concentration of  $HO_2^-$  anion.

Using the liquid jet apparatus at 10°C and a sodium hydroxide concentration of 3M, McCluskey estimated the overall transfer coefficient as  $10^{-7}$  g-mol/cm<sup>2</sup>-s torr [8].

Richardson et. al. [9] have performed static bulb experiments on chlorine gas absorption/reaction in aqueous solutions of NaOH, of  $H_2O_2$ , and of NaOH- $H_2O_2$ . Chlorine partial pressures were typically 5 torr or less. They monitored  $O_2$  and  $Cl_2$  gas phase concentrations as functions of time using a mass spectrometer. They found  $Cl_2$  absorption rates to be much higher with NaOH solutions than with NaOH- $H_2O_2$  solutions from which an  $O_2$  product must escape. This suggests a significant gas phase resistance to  $Cl_2$  absorption by alkaline hydrogen peroxide. Their data were consistent with a value for the pseudo-first order rate constant of reaction (4) greater than or equal to  $10^7$  M<sup>-1</sup> s<sup>-1</sup> at a 3.5 M  $HO_2^-$  concentration.

The production of singlet oxygen in a wetted-wall column reactor has been described (10). Higher yields of singlet oxygen are obtainable from this reactor than from sparger-type reactors since singlet deactivation via interaction with the liquid interface can be minimized. Depletion of peroxide anion near the interface can be a problem in wetted-wall reactors at high singlet oxygen production rates. The quenching of singlet oxygen produced within the liquid film was also discussed. Successful operation of the wetted-wall reactor at 45% singlet oxygen yield with over 80% utilization of reactants was reported.

The disproportionation reaction has been discussed in several publications (11-13). In concentrated hydrogen peroxide solutions, the rate of O<sub>2</sub> evolution is first order in hydrogen peroxide concentration. However, in alkaline hydrogen peroxide solutions the reaction mechanism changes and the rate of reaction is a more complicated function of peroxide and peroxide anion concentrations.

The equilibrium, shown below as reaction (9),

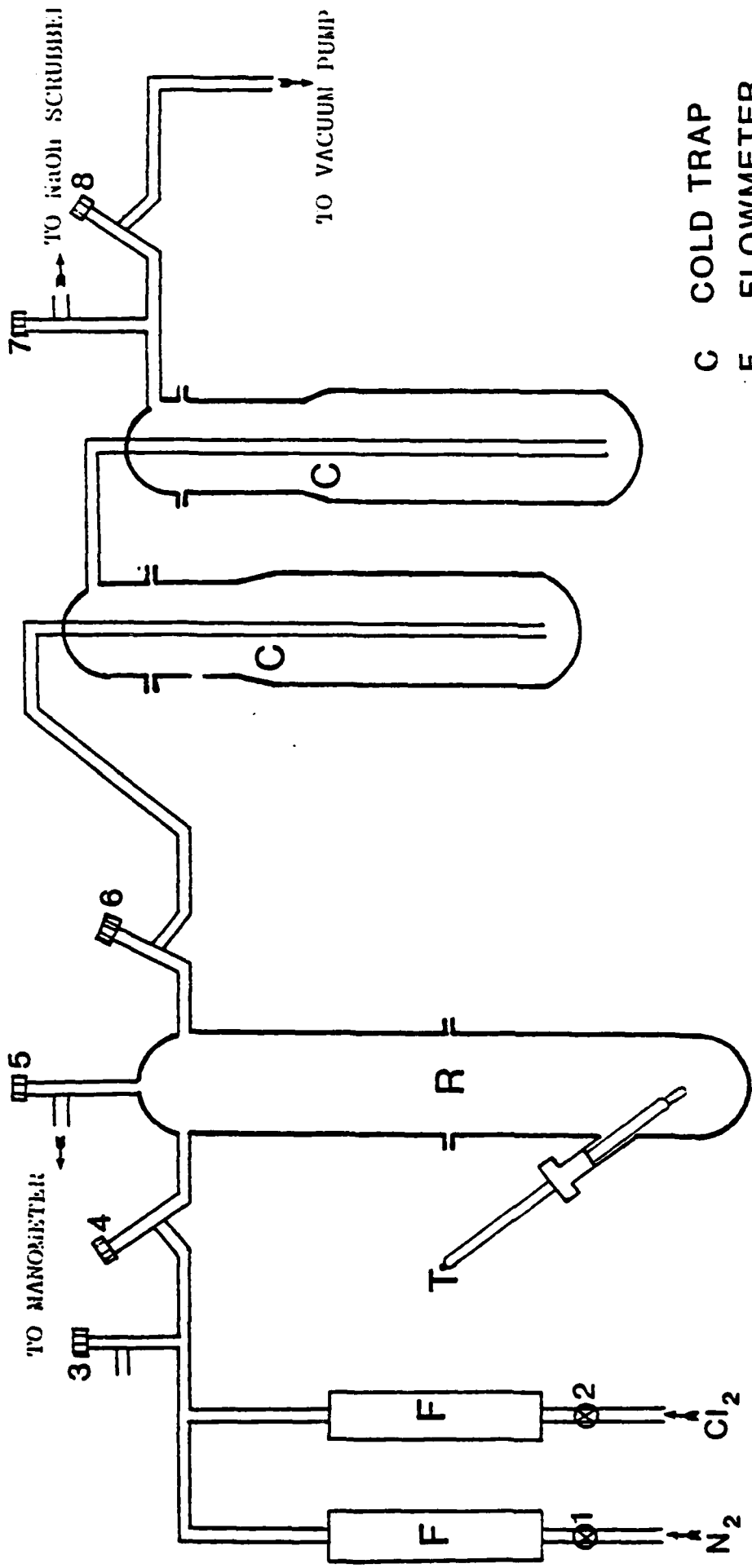


has also been described in a recent publication (14). Values of the equilibrium constant are presented for several temperatures between 15 and 35°C.

### Experimental Procedures

#### Apparatus

The experimental apparatus consists of a small glass reactor, with a thermometer attachment that is connected to the following equipment: gas [chlorine and nitrogen] feed lines, a manometer, and two cold traps in series with a mechanical vacuum pump. A detailed sketch of the apparatus is given in Figure 1. All surfaces that come into contact with the reactants are Pyrex glass or PTFE (Teflon). O-rings are of PTFE and the valves are glass-PTFE (Rotaflo). The almost-cylindrical glass reactor (2.9 cm x 40 cm) consists of a removable, vacuum-tight O-ring joint for transfer of solutions to and from the reactor. A PTFE adapter, carrying a PTFE-coated thermometer, fits into a ground joint attached to the lower part of the reactor. The thermometer is adjusted so that the bulb is fully immersed in the solution in the reactor. The reactor is cooled by a surrounding ice bath.



- C COLD TRAP
- F FLOWMETER
- 1-2 NEEDLE VALVE
- R REACTOR
- 3-8 ROTAFLO VALVE
- T THERMOMETER

Figure 1

A PTFE tube connects the manometer to the reactor through valve 7. The manometer fluid is mercury, covered with a layer of silicone oil to prevent attack by chlorine gas. Equal amounts of silicone oil are added to both the limbs to balance the pressure heads.

The entire system can be evacuated using a MARVAC (Cole-Parmer) mechanical vacuum pump. Over a 60 min. time period, the pressure increase in the sealed unit is less than 10 torr. Typical experiments lasted less than ten minutes.

Chlorine gas passes through the Matheson flowmeter tube (No. 602) to the chlorine line (PTFE) and is led into the reactor through valve 4. Needle valve 2 controls the flow rate of chlorine gas flowing out of the chlorine tank. The reactor can be isolated by closing valves 4 and 6. Unreacted chlorine gas is pulled into the cold traps maintained at liquid nitrogen temperature ( $-196^{\circ}\text{C}$ ). All condensed chlorine is carried to a caustic scrubbing unit through valve 7 using a purge of nitrogen. The scrubbing unit consists of two tanks in series, each filled with 5% NaOH solution. Vacuum can be released from the system by opening valve 3 to the atmosphere. Valve 8 serves to cut off the vacuum pump from the system.

**Chemicals Used:**

1. 30% Hydrogen Peroxide (Superoxol), Baker Analysed, Reagent, <1 ppm chloride ion.

2. Potassium hydroxide, Pellets, Baker Analyzed, Reagent, 0.0005% chloride ion.
3. 70% Nitric Acid, VWR Scientific Inc., Chemical Reagent, 0.5 ppm chloride ion.
4. Chlorine (gas), Matheson, Research grade, 99.96% purity.
5. Sodium Hydroxide, Pellets, Mallinckrodt Inc., Analytical Reagent, 98% purity.
6. d/j Reference electrode inner filling solution, Fisher Scientific (90-00-02).
7. d/j Reference electrode outer filling solution, 10%  $\text{KNO}_3$ , Fisher Scientific (90-00-03).
8. Sodium Chloride, crystal, Baker Analysed Reagent, 99.7% purity.

**Safety:**

Safety was of primary importance due to the hazards posed by the chemicals being handled. Safety equipment such as gloves, safety glasses, and apron were used throughout the experiment. The experiments were performed inside a safety hood with the exhaust fan always on.

**Preparation of Basic Peroxide Solution**

A known volume of 30%  $\text{H}_2\text{O}_2$  was added to a conical flask and was chilled in an ice-bath. A Teflon stirring bar was placed in the flask and a thermometer indicated the temperature. A known amount of 5N KOH was then added drop by drop to the chilled  $\text{H}_2\text{O}_2$  and the solution constantly stirred by a magnetic stirrer. The heat of mixing was absorbed by the ice-bath, and the temperature of the basic peroxide solution usually stabilized between 10 and 15°C. A large amount of water was kept at hand to quench the reaction in case it went out of control.

## Disproportionation Experiments

The basic peroxide solution was placed in the reactor, and the reactor sealed. The temperature of the solution was maintained at  $10 \pm 1$  °C. This temperature was chosen for convenience and safety considerations, i.e. minimizing the possibility of a runaway reaction. The liquid nitrogen cold traps were set in position. Adequate vacuum, as realized by continuous boiling of the basic peroxide solution, was pulled through the reactor. The reactor was isolated by closing valves 4 and 6, the initial pressure noted, and the stop watch started. The pressure in the reactor increased due to oxygen evolution via disproportionation. At regular time intervals, the pressure was recorded.

Disproportionation was studied with four different recipes. Table 1 lists the alkaline hydrogen peroxide solutions that were employed. The concentrations of peroxide and anions were calculated using an equilibrium constant for reaction (9) of 368.7 at 10° C. This was obtained by applying the van't Hoff relation, that  $\ln K$  is proportional to  $1/T$ , to the equilibrium data of reference (14).

### Reaction with Chlorine:

The solutions designated A and B in Table 1 were selected for study of their reaction with chlorine. These were chosen because the rates of disproportionation in the two solutions differed by over an order of magnitude while the concentrations of peroxide anion were almost the same (see Table 2 below). For each solution, different initial partial pressures of chlorine were examined for reaction times of: 1 minute, 3 minutes, and 6 minutes.

10°C was again chosen as the reaction temperature. The reactor was sealed after the addition of the basic peroxide solution. Valves 3 and 7 were kept closed, and valve 5 open. The temperature of the solution was

brought to  $8 \pm 1^\circ\text{C}$ . The liquid nitrogen cold traps were set in position and adequate vacuum drawn on the entire system. Valve 4 was closed cutting off the chlorine line (under vacuum) from the reactor. The reactor was isolated by closing valve 6, but the pump was kept running.

With the exhaust fan on and hood cover closed as far as possible, chlorine gas was passed cautiously into the chlorine line by manipulating needle valve 2. Valve 2 was then closed and the initial pressure in the reactor (of order 100 torr) recorded. The solution temperature was checked to be less than  $10^\circ\text{C}$ .

Valve 4 was then opened for a few seconds, and chlorine gas fed into the reactor. Valve 4 was then closed, a stop watch started, and the total pressure as indicated by the manometer recorded.

The reaction was found to be highly exothermic, and an immediate rise in temperature of the basic peroxide solution was observed. Manual control of the surrounding ice bath maintained the temperature at  $10 \pm 1^\circ\text{C}$ . Careful observation of the gas-liquid interface showed no special phenomenon. Small, rising bubbles of oxygen gas were always observed in the basic peroxide solution. The total pressure increased during the reaction by less than 10 torr.

During these experiments the volume of the gas phase was 230 ml, that of the liquid phase was 40 to 45 ml, and the cross-sectional area of the reactor, which would be the area of a quiescent interface, was  $6.61 \text{ cm}^2$ .

At the end of the desired reaction time (1 to 6 minutes) the final pressure was recorded and valve 6 opened. Unreacted chlorine was carried into the cold traps where it condensed. The vacuum pump was turned off and valve 8 closed. The line (PTFE) leading to the scrubbing unit was kept open to the atmosphere, and the system was vented to atmospheric pressure by



opening valve 7. The reactor contents were collected in a clean glass container for analysis.

Table 1 Alkaline Hydrogen Peroxide Solutions

	A	B	C	D
Vol (5N) KOH (ml)	25	30	15	40
Vol (30%) H <sub>2</sub> O <sub>2</sub> (ml)	20	10	25	30
H <sub>2</sub> O <sub>2</sub> (M)	1.69	0.175	4.24	1.47
H <sub>2</sub> O (M)	48.0	48.3	46.5	48.1
K <sup>+</sup> (M)	2.88	3.88	1.94	2.96
O <sub>2</sub> E <sup>-</sup> (M)	2.67	2.27	1.89	2.73
OH <sup>-</sup> (M)	0.21	1.61	0.05	0.23

All concentrations are based upon  $K_{eq} = 368.7$  at 10°C for reaction (9).

At the end of each run, all glassware was washed with copious amounts of water and rinsed thoroughly with distilled water.

Atmospheric pressure was measured each day by pulling vacuum through the system. The reactor background pressure was taken as the difference in vacuum drawn on the reactor immediately after liquid addition and the vacuum achieved when measuring the atmospheric pressure. This background pressure was normally 50-150 torr and was due to air, oxygen from disproportionation, and some water vapor. The chlorine partial pressure was taken as the change in reactor pressure upon addition of chlorine.

#### Analysis of Chloride Ion Concentration:

The chloride ion concentration was determined using an Orion 701 Ion Analyser with an Orion 94-17 chloride ion specific electrode and an Orion 900 double-junction reference electrode.

The Orion Instruction Manual for chloride ion specific electrodes mentions hydroxide ion ( $\text{OH}^-$ ) as an interferent for chloride ion measurement when the hydroxide ion is present in large concentration. No mention is made of perhydroxyl ion ( $\text{O}_2\text{H}^-$ ). Following a suggestion in the Orion manual, the basic peroxide solution was neutralized with nitric acid before analysis. Care was taken to avoid an excessive temperature rise during neutralization by cooling in an ice-bath and by adding a small amount of acid at a time. The operating pH range for the electrodes is 2-12.

#### Calibration of Electrodes:

The electrodes were checked for correct operation as suggested by the manual. A systematic procedure for calibration and a sample calibration curve were developed. The calibration curve did not vary significantly for a temperature range of 20-24°C.

### Analysis:

The first few attempts to measure the chloride ion concentration gave inconsistent results. A little experimentation showed that a small difference in the amount of acid added, from the amount used during calibration, caused large variations in the millivolt readings.

In view of this finding, the amount of nitric acid (5N) used for neutralization was the same as that used for calibration, (24 cc for solution A and 28 cc for solution B).

After neutralization with nitric acid, 1 ml of Ionic Strength Adjustor (5M  $\text{NaNO}_3$ ) was added to the reaction solution, the temperature was brought to  $22 \pm 2^\circ\text{C}$  and the millivolt reading was taken while the solutions were agitated by a magnetic stirrer. The analyzer was allowed to heat up for at least 15 minutes prior to each analysis. The electrodes were dipped in distilled water and blotted dry with a clean tissue after each millivolt measurement. Concentrations of chloride ion were read from the prepared millivolt-concentration calibration curve.

It was found that the chloride ion concentration measurement did not depend on the length of time for which the neutralized solutions were stored before analysis. Distilled water was used extensively for rinsing all glassware to minimize chloride ion contamination from external sources. The electrode filling solutions were changed every week for faster and more accurate response of the electrodes.

### Results

Experiments carried out to measure the rate of oxygen evolution via reaction (5) always gave linear pressure versus time plots. Table 2 presents the rate of pressure increase, obtained from linear least square fits to the pressure versus time data, as well as the corresponding rate of oxygen

production and the concentrations of reactants for each of the solutions examined. Disproportionation is the result of a free radical chain reaction. In reference (11) it is proposed that in alkaline hydrogen peroxide, chain initiation occurs through the  $\text{H}_3\text{O}_4^-$  ion that is in equilibrium with hydrogen peroxide and peroxide anion. For an unbranched chain reaction with second order termination, the rate of reaction is then

$$\frac{dn_{\text{O}_2}}{dt} = k([\text{H}_2\text{O}_2][\text{O}_2\text{H}^-])^{1/2}([\text{H}_2\text{O}_2] + [\text{O}_2\text{H}^-]) \quad (10)$$

The product of the square roots of peroxide and peroxide anion concentrations with the total peroxide concentration is shown in Table 2. It is clearly not proportional to the observed rate of oxygen production.

Plots of initial chlorine partial pressure versus the moles of chlorine reacted are presented in Figure 2 for solution A and in Figure 3 for solution B. Data for reaction times of one, three and six minutes are shown on each plot. In every case, there is a proportional increase in moles of chlorine reacted with an increase in initial chlorine partial pressure. This proportionality holds up to initial partial pressures of 150 to 200 torr. For any given reaction time, there is very little increase in the extent of reaction as the initial chlorine partial pressure increases beyond 200 torr. At higher initial chlorine partial pressures, increasing the reaction time from one to six minutes causes less than a 10% increase in the moles of chlorine reacted.

A solid line is sketched on each plot corresponding to 100% conversion of all chlorine added to the reactor. The data for lower initial chlorine partial pressures tend to parallel this line, but lie to its right. Since there cannot be greater than 100% conversion of chlorine to chloride ion there must be a consistent error. The values for the moles reacted at higher

Table 2 Disproportionation Rate Data

Solution	A	B	C	D
$[\text{H}_2\text{O}_2]$ (%)	1.69	0.175	4.24	1.47
$[\text{O}_2\text{H}^-]$ (%)	2.67	2.27	1.89	2.73
$dP/dt$ (torr/s)	0.129	0.0059	0.0641	0.163
$d_{\text{no}_2}/dt$ (mole/s $\times 10^6$ )	2.56	0.10	1.27	3.23
$([\text{H}_2\text{O}][\text{O}_2\text{H}^-])^{1/2}([\text{H}_2\text{O}_2] + [\text{O}_2\text{H}^-])$	9.3	1.5	17.4	8.4

initial partial pressures are highly reproducible. The chloride ion concentrations measured on solutions that do not undergo chlorine reaction correspond to negligible amounts of chloride ion. These considerations suggest the error lies either in the measurement of initial partial pressure or the solution volume.

After neutralization, the volume of solution was easily measured in a graduated cylinder that had been accurately calibrated by weight measurements. We estimate the error in this measurement to be less than 3%.

The chlorine experiments were performed in series, starting at the higher chlorine pressures. Chlorine in the gas feed line was not purged after each experiment, but was used in subsequent lower pressure runs. If back flow of residual air into the gas feed line occurred at the lower pressures, more chlorine would have entered the reactor than calculated from the change in system pressure. We believe this is the cause for the apparent error. The above considerations would not affect the results from the higher pressure experiments.

A comparison of Figures 2 and 3 shows that solution A, that has a much higher rate of disproportionation, gives only a slightly greater value for the limiting number of moles of chlorine reacted. This indicates that the results of these experiments are not sensitive to the disproportionation reaction.

Both Figures 2 and 3 show essentially complete conversion of all chlorine on a time scale of one minute up to a certain amount of reaction. After a critical amount of reaction occurs, say  $N$  moles of chlorine reacted, the reaction appears to turn off. The data show a very abrupt change from 100% conversion of all chlorine charged to almost no additional reaction beyond  $N$  moles. However, all activity in the reactor does not cease since additional reaction occurs for longer reaction times.

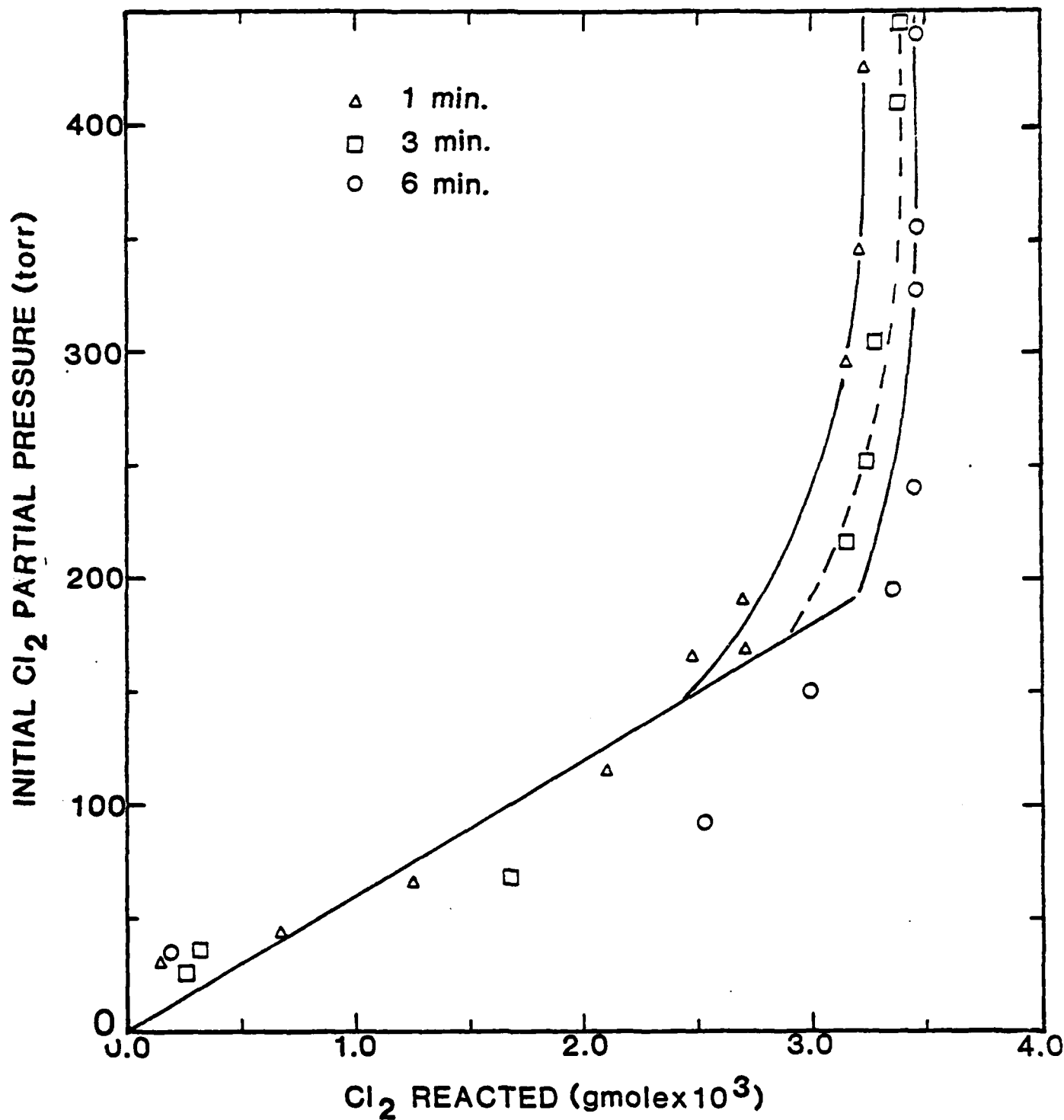


Figure 2

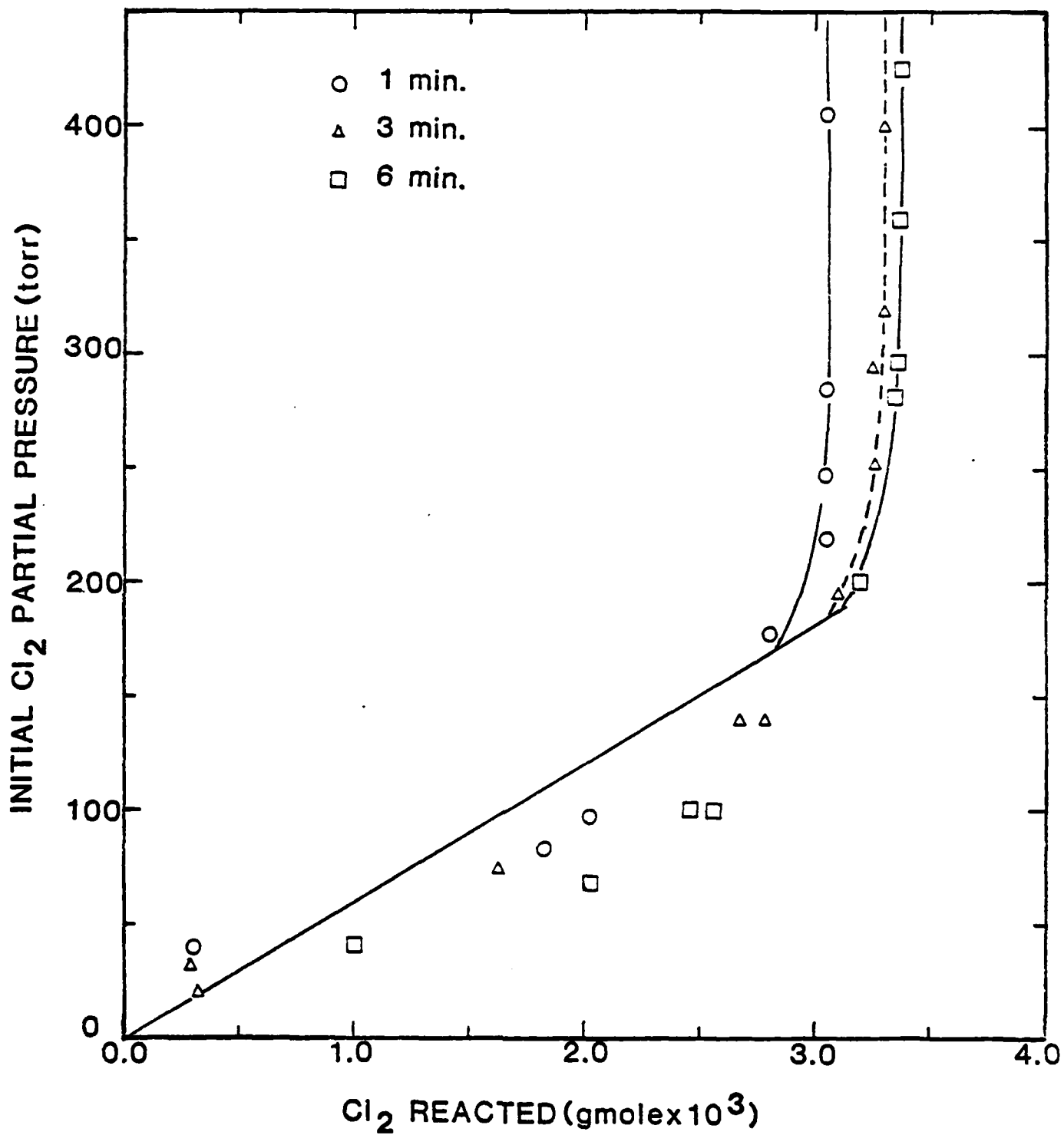


Figure 3



In summary, we see a very rapid reaction occurring until  $N$  moles of chlorine are consumed. After this, the amount of reaction is independent of the chlorine partial pressure and proceeds at a relatively slow rate. Furthermore, the chlorine reaction is insensitive to the rate of disproportionation.

### Discussion

The data of Figures 2 and 3 are consistent with a rapid reaction of chlorine with peroxide anion that initially occurs at or very close to the gas-liquid interface, but must occur at increasing depth beneath the interface as the liquid in the interfacial region becomes rich in chloride ion and depleted of peroxide anion.

If we treat the reaction as being instantaneous, the reaction will occur at a plane that is initially at the gas-liquid interface and which will move into the liquid phase only after all peroxide anion disappears from the interface. The assumption of an instantaneous rate of reaction greatly simplifies the differential equations describing mass transport with reaction, and it is reasonable in light of the high values that are estimated for the liquid phase reaction rate constant.

For a constant interfacial liquid phase concentration of chlorine, an instantaneous reaction rate, and a quiescent liquid, the depth of the reaction plane,  $\delta$ , will be

$$\delta = 2 \beta \sqrt{t} \quad (11)$$

and the molar absorption of chlorine per unit of interfacial area,  $Q$ , will be

$$Q = \frac{2 A^*}{\text{erf}(\beta/\sqrt{DA})} (DA t/\pi)^{1/2} \quad (12)$$

where  $\beta$  is a parameter defined by equation (13)

$$\exp [z^2/D_B] \operatorname{erfc} (z/\sqrt{D_B}) =$$

$$\frac{B_o}{2A^*} \left( \frac{D_B}{D_A} \right)^{1/2} \exp(z^2/D_A) \operatorname{erf}(z/\sqrt{D_A}) \quad (13)$$

$A^*$  is the constant liquid phase concentration of chlorine at the interface,

$D_A$  is the liquid phase diffusivity of chlorine,

$D_B$  is the liquid phase diffusivity of peroxide anion,

$t$  is time,

and  $E_o$  is the initial liquid phase concentration of peroxide anion. These equations are described in reference (6).

In our experiments the interfacial chlorine concentration is not constant but will decline as the amount of chlorine remaining in the vapor space falls. Nevertheless, if the rate of chlorine absorption falls sharply as the reaction plane moves away from the interface,  $A^*$  will remain approximately constant, and equations (11-13) will be applicable.

For large values of  $B_o/A^*$ ,

$$\frac{1}{\operatorname{erf} (z/\sqrt{D_A})} = \frac{B_o}{2A^*} \left( \frac{D_B}{D_A} \right)^{1/2} \quad (14)$$

Equation (12) then becomes

$$Q = E_o (D_B t/\pi)^{1/2} \quad (15)$$

and the rate of chlorine absorption is

$$dQ/dt = (D_B/\pi t)^{1/2} B_o/2 \quad (16)$$

Hence, the rate of reaction is independent of initial chlorine partial pressure and falls off as  $t^{-1/2}$ .

Using equation (15), an estimate of  $D_B$  can be obtained from knowledge

of the chlorine absorption at two different times.

$$D_B = \left[ (Q_2 - Q_1)/B_o (t_2^{1/2} - t_1^{1/2}) \right]^2 \quad (17)$$

The most significant information from Figures 2 and 3 is the moles of chlorine reacted at the point where less than complete conversion is achieved and the moles reacted when the extent of reaction is a function of time but is independent of initial partial pressure. This data is summarized in Table 3 where the information is presented in terms of moles of chlorine reacted per unit of interfacial area.

The diffusivity of peroxide anion given by equation (17) is also shown in Table 3. Values computed using the chlorine absorption for one and three minutes are shown along with those calculated from one and six minute absorption data. The magnitude of these diffusivities is large relative to typical liquid phase diffusion coefficients which are of order  $10^{-5} \text{ cm}^2/\text{s}$ . This suggests that molecular diffusion is not the sole mechanism for liquid phase mass transfer. Bubbles of oxygen from the disproportionation reaction always rise through the liquid, causing some convective transport. However, solutions A and B, that differ by over an order of magnitude in their rate of oxygen evolution, give similar diffusivities.

The data from one and three minute experiments give significantly larger diffusivities than the corresponding one and six minute results. This shows the rate of reaction is falling faster than suggested by equations (15) and (16). A possible explanation for this is a heat of reaction effect on the local rates of reaction and/or mass transfer. Equations (11 - 13) assume an instantaneous reaction and an isothermal liquid. Reaction (4) has a high heat of reaction. Should the heat released by the rapid initial interfacial reaction not be rapidly dissipated by solvent evaporation, there could exist a sharp thermal gradient in the vicinity of the interface. As the reaction

plane moves into the liquid, the lower temperatures would cause reductions in both the reaction rate constant and the diffusion coefficients.

The maximum amount of chlorine absorption for which there is essentially complete conversion may be used to define a depleted volume, which is the volume of solution that would be made void of peroxide anion by the rapid early reaction. This is illustrated in Table 3 in terms of a depleted depth,  $\delta_d$ , defined by

$$\delta_d = 2 Q_{\max} \text{ for 100\% conversion } / B_0 \quad (18)$$

The values of  $\delta_d$  given in Table 3 are rough measures of the depth of liquid that has peroxide anion concentration far below that of the bulk liquid when the surface concentration of that anion falls to zero.

If  $\delta_d$  is treated as the mean distance travelled by a peroxide anion in one minute, the shortest reaction time investigated, it can be used to estimate a diffusion coefficient.

$$D = \delta_d^2 / 2t \quad (19)$$

These values are also shown in Table 3. They are of the same magnitude as the diffusivities calculated from the liquid phase diffusion controlled reaction rate data using equation (17).

The magnitude of the peroxide anion diffusivity is an important parameter for fixing the liquid phase residence time or modeling the singlet oxygen production rate in liquid film reactors (10).

### Conclusions

When chlorine is reacted with alkaline hydrogen peroxide in an unagitated batch reactor there is a relatively rapid reaction that gives total conversion to chloride ion at small chlorine charges, but the percentage conversion of chlorine greatly declines when large amounts are

added to the reactor. With 10°C solutions approximately 2.5% in peroxide anion, and in which the rate of disproportionation is not too excessive, the extent of reaction becomes independent of the chlorine partial pressure after  $4.7 \times 10^{-4}$  moles of chlorine react per  $\text{cm}^2$  of interfacial area.

The extent of reaction data are qualitatively consistent with the theory of absorption with an instantaneous reaction (equations (11-13)), where the rate of chlorine absorption would become controlled by liquid phase diffusion of peroxide anion as soon as that anion's surface concentration falls to zero.

Data on the rate of reaction following the onset of liquid phase control, give values of approximately  $7 \times 10^{-4} \text{ cm}^2/\text{s}$  for the effective diffusivity of peroxide anion. This is much larger than typical liquid phase diffusivities. Convection due to the disproportionation reaction is not believed to be a factor since solutions whose oxygen evolution rate differed by over an order of magnitude gave similar effective diffusivities.

The rate of reaction in the liquid phase controlling region falls off faster in time than the  $1/t^{1/2}$  dependence predicted by theory.

In addition to giving information on the rate of liquid phase transport, batch reactor experiments are well suited for determining the rate of the disproportionation reaction. Our data suggest some modification is warranted to published equations describing the rate of this reaction.

Table 3 Data from Figures 2 and 3

Reactant solution	A	B
$C_{max}$ for 100% conversion ( $\text{mol Cl}_2/\text{cm}^2$ )	3.8-4.1	3.9-4.2
$Q_{p \rightarrow \infty}$ after 1 min	4.84	4.61
$Q_{p \rightarrow \infty}$ after 3 min	5.14	4.99
$Q_{p \rightarrow \infty}$ after 6 min	5.23	5.08
$D_B$ from 1 and 3 min data ( $\text{cm}^2/\text{s}$ )	$7.4 \times 10^{-4}$	$16.4 \times 10^{-4}$
$D_B$ from 1 and 6 min data ( $\text{cm}^2/\text{s}$ )	$3.2 \times 10^{-4}$	$6.4 \times 10^{-4}$
$\delta$ , depletion depth (cm)	0.30	0.36
$\delta^2/2t_{lmin}$ ( $\text{cm}^2/\text{s}$ )	$7.3 \times 10^{-4}$	$10.6 \times 10^{-4}$

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