PRELIMINARY KINETICS OF HIGH-TEMPERATURE REACTION
OF CHLORINE AND STEAM

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M. S. Thesis Submitted to Iowa State University

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Date Transmitted: June 1976

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MASTER

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ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82.

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MASTER

Preliminary kinetics of high-temperature reaction of chlorine and steam

by

Yu-sung Yeh

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Chemical Engineering and Nuclear Engineering
Major: Chemical Engineering

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1976

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NOMENCLATURE

a_A	activity of A at equilibrium
C_A^0	initial concentration of A (g-moles/ ℓ)
C_A	concentration of A (g-moles/ ℓ)
$C_{A,eq.}$	concentration of A at equilibrium (g-moles/ ℓ)
F_A^0	molal feed rate of A (g-moles/min.)
F_A	molal flow rate of A (g-moles/min.)
$K(K')$	equilibrium constant based on activity for Reaction I (Reaction II)
$K_{eq.}(K'_{eq.})$	equilibrium constant based on concentration for Reaction I (Reaction II)
M_A	mole-fraction of A at equilibrium
$N_1(N_2)$	molal feed ratio of H_2O to Cl_2 (Cl_2 to H_2O)
n_t	total number of moles of the gaseous mixture at equilibrium
n_A	number of moles of A at equilibrium
P	pressure (atm.)
R	gas constant (0.082 atm $\cdot$ ℓ /g-mole $\cdot$ $^{\circ}K$)
T	temperature ($^{\circ}K$)
V	volume (ℓ)
U	total volumetric flow rate (cc/min.)
U^0	initial total volumetric flow rate (cc/min.)
$x_{Cl_2}(x_{H_2O})$	fraction of Cl_2 (H_2O) converted into product when Cl_2 (H_2O) is the limiting species
$x_{Cl_2}^*(x_{H_2O}^*)$	conversion based on Cl_2 (H_2O) when H_2O (Cl_2) is limiting
$x_{Cl_2}^f(x_{H_2O}^f)$	final conversion of Cl_2 (H_2O) when Cl_2 (H_2O) is limiting

$\epsilon_{\text{Cl}_2}(\epsilon_{\text{H}_2\text{O}})$ fractional change in volume of the system between no conversion and complete conversion of Cl_2 (H_2O)

ν_{A} activity coefficient of A at equilibrium

subscript A component identifier (Cl_2 , HCl , H_2O , O_2)

ABSTRACT*

The kinetics of the reverse Deacon reaction, $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \frac{1}{2}\text{O}_2$, at 900 and 950K have been studied. A 6mm ID five-pass tubular vycor reactor with a volume of 34 c.c. was used for most of the runs and the space-time for those runs ranged from 2 to 7 seconds. A 25 mm ID one-pass reactor with a volume of 172 c.c. was also used but it gave much less satisfactory results because of flow problems. The space-time in this case ranged from 19 to 75 seconds. Twelve rate models were tested for the forward reaction. Only two of them ($k_1(\text{Cl}_2)$ and $k_1'(\text{Cl}_2)^2(\text{H}_2\text{O})$) gave reasonable correlation of the results. The values of k_1 obtained are 0.032 sec^{-1} at 900K and 0.051 sec^{-1} at 950K. The values of k_1' are $980 (\text{g-moles/l})^{-2} \text{ sec}^{-1}$ at 900K and $1760 (\text{g-moles/l})^{-2} \text{ sec}^{-1}$ at 950K.

*USERDA Report IS-T-717. This work was performed under Contract

W-7405-eng-82 with the Energy Research and Development Administration.

INTRODUCTION

Recently, people have begun to realize that the remaining energy reserves on this planet will become far too valuable as feedstocks for chemical production to be simply burned for their energy content. In the search for alternative energy sources, many scientists and engineers think hydrogen will be the answer. Hydrogen will be relatively cheap, abundant, and clean (7, 9, 15, 21, 29, 36, 39, 54, 57).

Hydrogen is currently a major industrial chemical serving primarily as a chemical intermediate in the production of hydrogen-containing substances such as ammonia, methanol, and refined petroleum products.

There have been numerous papers published on the subject of the possible uses of hydrogen as a fuel. Hydrogen is particularly attractive for use in fuel cells. It could also be used in any type of combustion engine, although some modification of conventional designs would be required (48). The major problems involved in using hydrogen as a common fuel are storage and transportation. Several scientists have researched this subject extensively (8, 21, 28, 36, 53).

Another major problem is that the securing of abundant supplies of pure hydrogen presents difficult technical problems. Most of the hydrogen produced currently in the United States and Europe is made by the steam reforming of natural gas or by the partial oxidation of oil. But the decreasing petroleum reserves in the next decade may make it necessary to adopt alternative methods of generation. Hydrogen can be formed by decomposing water. Direct thermal decomposition by heat

occurs only at such high temperature that it is impractical to consider this as an engineering process (47).

The major candidate technologies for this century include electrolysis, new open-cycle thermochemical processes based on fossil fuel feedstocks (44, 50), and closed-cycle thermochemical generation methods (12). Longer range possibilities include biological and photolytic methods. Although electrolysis is the best developed of these technologies at present, cost estimates for hydrogen production by the above approaches indicate that electrolysis will probably not be the generally preferred method for large scale production unless off-peak electricity costs of under 5 mills per kilowatt-hour are available. Because pollution standards will become more strict and fossil fuel more expensive, the open-cycle processes seem to be less feasible for the future than the closed-cycle processes (54).

Several closed-cycle thermochemical processes have been reported (1, 6, 9, 22, 35). The processes, which ideally use water and heat and produce only hydrogen, oxygen, and degraded heat, involve the reactions of water with certain chemical compounds in a specified sequence at low temperatures. Ideally all the intermediates will be recycled within the system, but losses of recyclable species will still occur in a large-scale production process. That is going to cause some economic and environmental impact on the closed-cycle processes (10).

Computerized methods, used to sort out the thermodynamically sound reactions for the closed-cycle water-splitting processes, have also been devised (22). Up to now, most of the work has been done in

understanding the basic chemistry, the thermodynamics and the processing characteristics.

The chemical reactions involved in the closed-cycle processes can be classified according to three essential functions: (a) water binding, (b) product recovery, and (c) reagent regeneration. A single reaction step can perform a dual function as in the reverse Deacon reaction, $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$, in which the water binding reaction is combined with the oxygen recovery. That is why some of the reported processes have been built around the reverse Deacon reaction. For example, the iron chloride process, which was suggested by DeBeni (18),

Others are shown in Appendix A.

The equilibrium conversion of the reverse Deacon reaction is 50.5% at 900°K and 55% at 950°K for equal-molal feed. Although the thermodynamics of this reaction are well known, the kinetics have not been studied thoroughly. The purpose of this study is to determine the reaction kinetics necessary for a comparative evaluation of the closed-cycle thermochemical water-splitting processes.

LITERATURE REVIEW

The oxidation of hydrochloric acid, which is called the Deacon reaction, has been of commercial interest since 1868 for manufacture of chlorine (38, 49). The Deacon reaction, which was the first large scale gas-phase catalytic process used by the chemical industry, enjoyed wide usage in Europe but was never commercially practiced in the U.S.A. There have been a lot of patents issued regarding the catalysts and the operating conditions for the Deacon reaction (16).

Falckenstein (20) discussed the equilibrium constants for both the Deacon reaction and the reverse Deacon reaction. Arnold and Kobe (2) wrote the following equation for calculating the equilibrium constant of $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$:

$$\log K = \frac{5881.7}{T} - 0.93035 \log T + (1.3704 \times 10^{-5})T - (1.7581 \times 10^{-8})T^2 - 4.1744 \quad (1)$$

Johnstone (33) also published the free energy data for the Deacon reaction.

Jones (34) wrote his Ph.D. dissertation on the kinetics of the oxidation of hydrogen chloride. The three temperatures he used were 598, 613, and 628°K. He also studied the reverse Deacon reaction at 628 and 643°K. His experiments were based on the heterogeneous catalytic reaction.

Few papers, most of them published before 1940, discussed the formation of hydrochloric acid (or hydrogen chloride) via the reverse Deacon reaction. Hirschkind (31) studied the reaction and gave a

history of the attempts to utilize this reaction. He also stated that in order to make the reaction commercially practicable, a reducing agent such as carbon must be used to combine with the oxygen liberated by the reaction. Other authors also made the same argument (14, 26, 32, 41, 43).

Barstow and Heath (4) have a patent for the equi-molal proportions of chlorine and steam reacted at 1000-1600°C in the substantial absence of reducing substances. Apparatus and various details of operation were described. Reference (11) also discusses running the reaction without a reducing agent. Ohkawa (40) has a patent to use ultraviolet light to make the dissolved chlorine react with the water to form hydrochloric acid.

Shelud'ko (51) used a catalyst containing 20% of MgO, 25% of MgCl_2 , and 25% of CaO to obtain a 97% yield of hydrogen chloride for reverse Deacon reaction at 900°C.

Euratom scientists have proposed a pilot plant reactor design to study the kinetics of the reverse Deacon reaction. Similar reactors have also been described by Musso in (19) and by Funk and Reinstrom (23). The proposed apparatus includes reaction and analytical sections.

The reaction section can be divided into the preheaters, the mixing chamber, and the reactor. Concentrated solutions of potassium iodide are used to trap the unreacted chlorine. Oxygen is determined by a gas chromatograph.

No one has obtained data which indicate either an empirical rate equation or a satisfactory mechanism. That information is needed for the calculation of the reactor size.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

Figure 1 illustrates the equipment setup used to study the chlorine reaction with steam. The chlorine gas cylinder was purchased from Matheson Gas Company and fitted with Matheson's model B-15 regulator. Penntube's 1/4" flexible corrugated Teflon tube was used to connect the chlorine cylinder, the rotameter and the chlorine preheater. The rotameter, specially designed to handle chlorine, was purchased from Emerson Electric Co. The flow rate range is from 8 to 130 standard cc/min. Figure 2 illustrates the steam generator. The generator was made of stainless steel and was wrapped with a 1" x 72" heavily insulated fibrous glass flexible electric heating tape. The heat input to the steam generator was controlled by a power-stat. A 30# pressure gauge indicated the pressure in the steam generator. The control of the steam flow rates was achieved by using a 8513A Brooks' NRS needle valve with a numerical handle. Pope's 9 mm ID Flo-Tite heat shrinkable tube was used to connect the steam generator and the steam preheater. Another heating tape, controlled by a temperature controller, was wrapped along the line from steam valve to steam preheater to prevent steam from condensing. The temperature of the heating tape was controlled around 180°C.

The preheaters, reactor and water scrubber were made of Vycor tube. Figure 3 illustrates their size and arrangement. Two kinds of reactor were used. One was a five-pass 34 cc reactor as shown in Figure 3. The other was a 25 mm ID 35 cm long one-pass 172 cc reactor. The preheaters were put in two 7" long 1-1/4" ID Clam-shell furnaces. The

Figure 1. Experimental apparatus

Figure 2. Steam generator

Figure 3. The preheaters, five-pass reactor, and water scrubber

reactor was put in a 13" long 1-1/4" ID Clam-shell furnace. The furnace temperatures were on-off controlled by Honeywell's Brown Protect-O-Vane temperature controller. The Alumel-Chromel thermocouples were put in the center of the furnace. A Leeds & Northrup's millivolt potentiometer was used to calibrate the temperature controller. A Cole-Parmer Instrument Company's variable speed masterflex tubing pump was used to recycle the water in the scrubber. 1/4" Tygon tube was used in the pump line.

The pass from reactor to scrubber was designed so that the product stream could be quenched as fast as possible to prevent a reverse reaction. Glass beads were put in the scrubber to give better contact between gas stream and water. 1/4" Tygon tube connected the outlet of the scrubber to a U-shaped pyrex tube. The pyrex tube was immersed in a pyrex jar partly filled with concentrated KI solution.

The line between the preheaters and reactors was wrapped with glass wool insulation material and was directly heated by an infra-red lamp. The temperatures of the preheater-furnaces were always controlled around 150°C higher than the reactor-furnace. There existed a temperature drop from the preheaters to the mixing zone. The above arrangements were designed to insure that the temperature of the gas mixture would be very close to the reactor-furnace temperature when the mixture reached the reactor.

The steam generator and furnaces were heated first. When the pressure in the steam generator reached the required level, the steam valve was opened to let the steam into the system. For each experiment, which usually ran for four hours, the steam valve was set at a fixed opening. Then the chlorine valve was opened. The steam generator

was weighed before and after each experiment. The weight difference divided by the steam valve operating time was the mass flow rate of steam. Ideal gas law was used to convert the mass flow rates into volumetric flow rates. The results were double-checked with the steam table.

It usually took thirty minutes for the whole system to reach steady state. Then a timer and an inverted graduated cylinder filled with KI solution were used to measure the oxygen evolution rates. Oxygen, hydrochloric acid, unreacted steam and chlorine were present in the product gas stream. The scrubber condensed the steam and absorbed the hydrochloric acid and some chlorine gas. Only oxygen and chlorine entered the U-shaped tube. Then chlorine reacted with potassium iodide ($\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$, $\text{I}_2 + \text{I}^- \longrightarrow \text{I}_3^-$) (55), so that oxygen was the only gas entering the inverse graduated cylinder. The gas volume in the inverse graduated cylinder was recorded every five minutes. The average oxygen evolution rates were calculated. Usually each run lasted for thirty minutes. The chlorine flow rate was then adjusted to a new value. It took roughly another thirty minutes for the system to regain steady state. During each experiment, the steam flow rate was fixed. The space-time was varied only by changing the chlorine flow rate.

THEORY

Design Equation for Steady-State Plug Flow Reactor (37)

Three assumptions were made for the reactor. First, there was to be no mixing in the axial direction (the direction of flow). Second, there was to be complete mixing in the radial direction. Third, there would be a uniform velocity across the radius. The reactor met the criteria of a plug flow reactor (52). The deviations from the plug flow assumptions will be discussed later (p. 49).

In a plug flow reactor the composition of the fluid varies from point to point along a flow path. Consequently, the material balance for a reaction component must be made for a differential element of volume dV .

$$\text{Input} = \text{Output} + \text{Disappearance by Reaction} \quad (2)$$

Referring to Figure 4:

$$\text{Input of A} = F_A;$$

$$\text{Output of A} = F_A + dF_A;$$

$$\text{Disappearance of A by reaction (moles/time)}$$

$$= (-r_A)dV = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluids})} \right)$$

$$\times (\text{volume of differential element});$$

So Equation (2) becomes

$$F_A = (F_A + dF_A) + (-r_A)dV \quad (3)$$

Because

C_A : CONCENTRATION OF A (moles/volume)

F_A : MOLAL FLOW RATE OF A (moles/time)

X_A : FRACTION OF A CONVERTED INTO PRODUCT

V : TOTAL VOLUMETRIC FLOW RATE (volume/time)

SUPERScript o : CONDITIONS AT THE ENTRANCE

SUPERScript f : CONDITIONS AT THE EXIT

Figure 4. Notation for a plug flow reactor

$$F_A = F_{Ao}(1 - X_A);$$

and

$$dF_A = d[F_{Ao}(1 - X_A)] = -F_{Ao}dX_A; \quad (4)$$

Equations (3) and (4) can be combined to give

$$F_{Ao}dX_A = (-r_A)dV \quad (5)$$

This is the equation accounting for A in the differential section of reactor of volume dV . For the reactor as a whole, Equation (5) must be integrated.

$$\int_0^V \frac{dV}{F_{Ao}} = \int_0^{X_A^f} \frac{dX_A}{(-r_A)}$$

Since F_{Ao} is a constant,

$$\frac{V}{F_{Ao}} = \int_0^{X_A^f} \frac{dX_A}{(-r_A)}$$

and

$$F_{Ao} = U_o C_{Ao}^o$$

Therefore, τ = space-time = time required to process one reactor volume

$$\text{of feed} = \frac{V}{U_o} = \frac{F_{Ao}^o}{U_o} \int_0^{X_A^f} \frac{dX_A}{(-r_A)} = C_{Ao}^o \int_0^{X_A^f} \frac{dX_A}{(-r_A)} \quad (6)$$

Concentration of Each Species Present in the System

The reverse Deacon reaction may be written in either of the following two forms:

1. If chlorine is the limiting species:

$$N_1 = \frac{F_{\text{H}_2\text{O}}^0}{F_{\text{Cl}_2}^0} = \frac{C_{\text{H}_2\text{O}}^0}{C_{\text{Cl}_2}^0} \quad (7)$$

$$\epsilon_{\text{Cl}_2} = \frac{U_{X_{\text{Cl}_2}=1} - U_{X_{\text{Cl}_2}=0}}{U_{X_{\text{Cl}_2}=0}} = \frac{(F_{\text{H}_2\text{O}}^0 - F_{\text{Cl}_2}^0 + 2F_{\text{Cl}_2}^0 + \frac{1}{2} F_{\text{Cl}_2}^0) - (F_{\text{Cl}_2}^0 + F_{\text{H}_2\text{O}}^0)}{(F_{\text{Cl}_2}^0 + F_{\text{H}_2\text{O}}^0)}$$

$$= \frac{F_{\text{Cl}_2}^0}{2(F_{\text{Cl}_2}^0 + F_{\text{H}_2\text{O}}^0)} = \frac{1}{2(1 + N_1)} \quad (8)$$

$$X_{\text{Cl}_2} = 1 - \frac{C_{\text{Cl}_2}}{C_{\text{Cl}_2}^0} \quad (9)$$

$$U = U_o [1 + \epsilon_{\text{Cl}_2} X_{\text{Cl}_2}] = U_o \left[1 + \frac{X_{\text{Cl}_2}}{2(1 + N_1)} \right] = U_o \left[\frac{2(N_1 + 1) + X_{\text{Cl}_2}}{2(N_1 + 1)} \right] \quad (10)$$

$$C_{\text{Cl}_2} = \frac{F_{\text{Cl}_2}}{U} = \frac{F_{\text{Cl}_2}^0 (1 - X_{\text{Cl}_2})}{\frac{2(N_1 + 1) + X_{\text{Cl}_2}}{2(N_1 + 1)} U_o} = \frac{2C_{\text{Cl}_2}^0 (N_1 + 1) (1 - X_{\text{Cl}_2})}{2(N_1 + 1) + X_{\text{Cl}_2}} \quad (11)$$

$$C_{\text{H}_2\text{O}} = \frac{F_{\text{H}_2\text{O}}}{U} = \frac{F_{\text{H}_2\text{O}}^0 - F_{\text{Cl}_2}^0 X_{\text{Cl}_2}}{\frac{2(N_1 + 1) + X_{\text{Cl}_2}}{2(N_1 + 1)} U_o} = \frac{2C_{\text{Cl}_2}^0 (N_1 + 1) (N_1 - X_{\text{Cl}_2})}{2(N_1 + 1) + X_{\text{Cl}_2}} \quad (12)$$

$$C_{HCl} = \frac{2F_{Cl_2}^o X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} = \frac{4C_{Cl_2}^o (N_1 + 1)X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} \quad (13)$$

$$U_o \left[\frac{2(N_1 + 1)}{2(N_1 + 1)} \right]$$

$$C_{O_2} = \frac{\frac{1}{2} F_{Cl_2}^o X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} = \frac{C_{Cl_2}^o (N_1 + 1)X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} \quad (14)$$

$$U_o \left[\frac{2(N_1 + 1)}{2(N_1 + 1)} \right]$$

$$X_{H_2O}^* = \frac{C_{Cl_2}^o X_{Cl_2}}{C_{H_2O}^o} = \frac{X_{Cl_2}}{N_1} \quad (15)$$

2. If steam is the limiting species:

$$N_2 = \frac{F_{Cl_2}^o}{F_{H_2O}^o} = \frac{C_{Cl_2}^o}{C_{H_2O}^o} \quad (16)$$

$$\epsilon_{H_2O} = \frac{U_{X_{H_2O}=1} - U_{X_{H_2O}=0}}{U_{X_{H_2O}=0}} = \frac{(F_{Cl_2}^o - F_{H_2O}^o + 2F_{H_2O}^o + \frac{1}{2} F_{H_2O}^o) - (F_{H_2O}^o + F_{Cl_2}^o)}{(F_{H_2O}^o + F_{Cl_2}^o)}$$

$$= \frac{F_{H_2O}^o}{2(F_{H_2O}^o + F_{Cl_2}^o)} = \frac{1}{2(1 + N_2)} \quad (17)$$

$$X_{H_2O} = 1 - \frac{C_{H_2O}}{C_{H_2O}^o} \quad (18)$$

$$U = U_o [1 + \epsilon_{H_2O} X_{H_2O}] = U_o \left[1 + \frac{X_{H_2O}}{2(1 + N_2)} \right] = U_o \left[\frac{2(N_2 + 1) + X_{H_2O}}{2(N_2 + 1)} \right] \quad (19)$$

$$C_{Cl_2} = \frac{F_{Cl_2}}{U} = \frac{F_{Cl_2}^0 - F_{H_2O}^0 X_{H_2O}}{2(N_2 + 1) + X_{H_2O}} = \frac{2C_{H_2O}^0 (N_2 + 1)(N_2 - X_{H_2O})}{2(N_2 + 1) + X_{H_2O}} \quad (20)$$

$$U_o \left[\frac{1}{2(N_2 + 1)} \right]$$

$$C_{H_2O} = \frac{F_{H_2O}}{U} = \frac{F_{H_2O}^0 (1 - X_{H_2O})}{2(N_2 + 1) + X_{H_2O}} = \frac{2C_{H_2O}^0 (N_2 + 1)(1 - X_{H_2O})}{2(N_2 + 1) + X_{H_2O}} \quad (21)$$

$$U_o \left[\frac{1}{2(N_2 + 1)} \right]$$

$$C_{HCl} = \frac{2F_{H_2O}^0 X_{H_2O}}{2(N_2 + 1) + X_{H_2O}} = \frac{4C_{H_2O}^0 (N_2 + 1)X_{H_2O}}{2(N_2 + 1) + X_{H_2O}} \quad (22)$$

$$U_o \left[\frac{1}{2(N_2 + 1)} \right]$$

$$C_{O_2} = \frac{\frac{1}{2} F_{H_2O}^0 X_{H_2O}}{2(N_2 + 1) + X_{H_2O}} = \frac{C_{H_2O}^0 (N_2 + 1)X_{H_2O}}{2(N_2 + 1) + X_{H_2O}} \quad (23)$$

$$U_o \left[\frac{1}{2(N_2 + 1)} \right]$$

$$X_{Cl_2}^* = \frac{C_{H_2O}^0 X_{H_2O}}{C_{Cl_2}^0} = \frac{X_{H_2O}}{N_2} \quad (24)$$

Rate and Design Equations Neglecting Reverse Reaction

If the reverse reactions of Reactions I and II can be neglected, the reaction rate equations are:

$$\text{Rate} = (-r_{Cl_2}) = (-r_{H_2O}) = k_1 C_{Cl_2}^a \cdot C_{H_2O}^b \text{ for Reaction I} \quad (25)$$

$$\text{Rate} = (-r_{Cl_2}) = (-r_{H_2O}) = k_1' C_{Cl_2}^a \cdot C_{H_2O}^b \text{ for Reaction II} \quad (26)$$

1. If chlorine is the limiting species:

The derivation for Reaction II is the same as the following derivation, except k_1' should be used instead of k_1 .

Equation (6) becomes

$$\tau = C_{Cl_2}^o \int_0^{x_{Cl_2}^f} \frac{dx_{Cl_2}}{(-r_{Cl_2})} \quad (27)$$

Inserting Equations (11) and (12) into Equation (25) gives

$$\begin{aligned} (-r_{Cl_2}) &= k_1 \left[\frac{2C_{Cl_2}^o (N_1 + 1)(1 - x_{Cl_2})}{2(N_1 + 1) + x_{Cl_2}} \right]^a \left[\frac{2C_{Cl_2}^o (N_1 + 1)(N_1 - x_{Cl_2})}{2(N_1 + 1) + x_{Cl_2}} \right]^b \\ &= k_1 [C_{Cl_2}^o]^{a+b} \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + x_A} \right]^{a+b} (1 - x_{Cl_2})^a \cdot (N_1 - x_{Cl_2})^b \end{aligned} \quad (28)$$

Combining Equations (27) and (28) gives

$$\begin{aligned} \tau &= C_{Cl_2}^o \int_0^{x_{Cl_2}^f} \frac{dx_{Cl_2}}{k_1 [C_{Cl_2}^o]^{a+b} \cdot \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + x_{Cl_2}} \right]^{a+b} \cdot (1 - x_{Cl_2})^a \cdot (N_1 - x_{Cl_2})^b} \end{aligned} \quad (29)$$

2. If steam is the limiting species:

The derivation for Reaction II is the same as the following derivation, except k_1' should be used instead of k_1 .

Equation (6) becomes

$$\tau = C_{H_2O}^o \int_0^{x_{H_2O}^f} \frac{dx_{H_2O}}{(-r_{H_2O})} \quad (30)$$

Inserting Equations (20) and (21) into Equation (25) gives

$$\begin{aligned} (-r_{H_2O}) &= k_1 \cdot \left[\frac{2C_{H_2O}^o (N_2 + 1) (N_2 - x_{H_2O})}{2(N_2 + 1) + x_{H_2O}} \right]^a \\ &\quad \cdot \left[\frac{2C_{H_2O}^o (N_2 + 1) (1 - x_{H_2O})}{2(N_2 + 1) + x_{H_2O}} \right]^b \\ &= k_1 \cdot [C_{H_2O}^o]^{a+b} \cdot \left[\frac{2(N_2 + 1)}{2(N_2 + 1) + x_{H_2O}} \right]^{a+b} \cdot (N_2 - x_{H_2O})^a \cdot (1 - x_{H_2O})^b \end{aligned} \quad (31)$$

Combining Equations (30) and (31) gives

$$\begin{aligned} \tau &= C_{H_2O}^o \int_0^{x_{H_2O}^f} \frac{dx_{H_2O}}{k_1 [C_{H_2O}^o]^{a+b} \cdot \left[\frac{2(N_2 + 1)}{2(N_2 + 1) + x_{H_2O}} \right]^{a+b} \cdot (N_2 - x_{H_2O})^a \cdot (1 - x_{H_2O})^b} \end{aligned} \quad (32)$$

3. Comparison of Equations (29) and (32):

The following derivation will prove that Equation (32) is actually a different form of Equation (29).

Combining Equations (7), (15), and (29) gives

$$\begin{aligned}
\tau &= \frac{C_{H_2O}^o}{N_1} \int_0^{(X_{H_2O}^*)^f} \frac{N_1 \cdot dX_{H_2O}^*}{k_1 \cdot \left(\frac{C_{H_2O}^o}{N_1}\right)^{a+b} \cdot \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + N_1 X_{H_2O}^*}\right]^{a+b} \cdot (1 - N_1 X_{H_2O}^*)^a \cdot (N_1 - N_1 X_{H_2O}^*)^b} \\
&= \frac{C_{H_2O}^o}{N_1} \int_0^{(X_{H_2O}^*)^f} \frac{N_1^a \cdot N_1 \cdot dX_{H_2O}^*}{k_1 \cdot (C_{H_2O}^o)^{a+b} \cdot \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + N_1 X_{H_2O}^*}\right]^{a+b} \cdot (1 - N_1 X_{H_2O}^*)^a \cdot (1 - X_{H_2O}^*)^b}
\end{aligned}
\tag{33}$$

Combining Equations (7) and (16) gives

$$N_1 = \frac{1}{N_2} \tag{34}$$

Inserting Equation (34) into Equation (33) gives

$$\begin{aligned}
\tau &= C_{H_2O}^o \int_0^{(X_{H_2O}^*)^f} \frac{dX_{H_2O}^*}{k_1 \cdot (C_{H_2O}^o)^{a+b} \cdot \left[\frac{2(N_2 + 1)}{2(N_2 + 1) + X_{H_2O}^*}\right]^{a+b} \cdot (N_2 - X_{H_2O}^*)^a \cdot (1 - X_{H_2O}^*)^b}
\end{aligned}
\tag{35}$$

From Equation (15),

$$x_{H_2O}^* = \frac{C_{Cl_2}^o}{C_{H_2O}^o} \cdot x_{Cl_2} = \frac{C_{Cl_2}^o}{C_{H_2O}^o} \cdot \frac{2U_{O_2}}{U_{Cl_2}^o} \quad (36)$$

And

$$x_{H_2O} = \frac{2U_{O_2}}{U_{H_2O}^o} \quad (37)$$

Applying the ideal gas law,

$$C_{Cl_2}^o = \frac{P_{Cl_2}^o}{RT} = \frac{P_t \cdot \left(\frac{U_{Cl_2}^o}{U_{H_2O}^o + U_{Cl_2}^o} \right)}{RT} \quad (38)$$

$$C_{H_2O}^o = \frac{P_{H_2O}^o}{RT} = \frac{P_t \cdot \left(\frac{U_{H_2O}^o}{U_{H_2O}^o + U_{Cl_2}^o} \right)}{RT} \quad (39)$$

Dividing Equation (38) by Equation (39) gives

$$\frac{C_{Cl_2}^o}{C_{H_2O}^o} = \frac{U_{Cl_2}^o}{U_{H_2O}^o} \quad (40)$$

Combining Equations (36), (37), and (40) gives

$$x_{H_2O} = x_{H_2O}^* \quad (41)$$

Then Equation (35) becomes exactly the same as Equation (32).

Therefore, when Equation (32) is applied to the steam-limiting cases the results are the same as applying Equation (35).

Two Special Cases of the Design Equations Neglecting Reverse Reaction.

1. $a = 1, b = 0$

This could happen to both Reactions I and II. The derivation for Reaction II is the same as the following derivation except k'_1 should be used instead of k_1 .

Equation (29) becomes

$$\begin{aligned}\tau &= C_{Cl_2}^o \int_0^{X_{Cl_2}^f} \frac{dX_{Cl_2}}{k_1 \cdot C_{Cl_2}^o \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + X_{Cl_2}} \right] \cdot (1 - X_{Cl_2})} \\ &= \frac{1}{2k_1(N_1 + 1)} \int_0^{X_{Cl_2}^f} \left[-1 + \frac{2N_1 + 3}{1 - X_{Cl_2}} \right] dX_{Cl_2} \\ &= \frac{-X_{Cl_2}^f - (2N_1 + 3)\ln(1 - X_{Cl_2}^f)}{2k_1(N_1 + 1)}\end{aligned}\quad (42)$$

$$\text{Let } X = \frac{-X_{Cl_2}^f - (2N_1 + 3)\ln(1 - X_{Cl_2}^f)}{2(N_1 + 1)}\quad (43)$$

$$\text{Then } X = k_1 \tau\quad (44)$$

2. $a = 2, b = 1$

This could only happen to Reaction II.

Equation (29) becomes

$$\tau = C_{Cl_2}^o \int_0^{X_{Cl_2}^f} \frac{dX_{Cl_2}}{k'_1 \cdot (C_{Cl_2}^o)^3 \cdot \left[\frac{2(N_1 + 1)}{2(N_1 + 1) + X_{Cl_2}} \right]^3 \cdot (1 - X_{Cl_2})^2 \cdot (N_1 - X_{Cl_2})}$$

$$= \frac{1}{k_1' \cdot [C_{Cl_2}^o]^2 \cdot [2(N_1 + 1)]^3} \int_0^{X_{Cl_2}^f} \frac{(7N_1 + 8)X_{Cl_2}^2 + (12N_1^2 + 22N_1 + 11)X_{Cl_2} + (8N_1^3 + 24N_1^2 + 25N_1 + 8)}{[1 + \frac{(1 - X_{Cl_2})^2 (N_1 - X_{Cl_2})}{(1 - X_{Cl_2})^2 (N_1 - X_{Cl_2})}]^3} dX_{Cl_2}$$

$$= \frac{1}{k_1' \cdot [C_{Cl_2}^o]^2 [2(N_1 + 1)]^3} \left\{ -X_{Cl_2}^f + \frac{20N_1^3 + 60N_1^2 + 45N_1}{(N_1 - 1)^2} \ln(1 - X_{Cl_2}^f) + \frac{8N_1^3 + 36N_1^2 + 54N_1 + 27}{N_1 - 1} \left(\frac{X_{Cl_2}^f}{1 - X_{Cl_2}^f} \right) - \frac{27N_1^3 + 54N_1^2 + 36N_1 + 8}{(N_1 - 1)^2} \ln\left(\frac{N_1 - X_{Cl_2}^f}{N_1}\right) \right\} \quad (45)$$

Let

$$X = \frac{1}{[C_{Cl_2}^o]^2 \cdot [2(N_1 + 1)]^3} \left\{ -X_{Cl_2}^f + \frac{5N_1(2N_1 + 3)^2}{(N_1 - 1)^2} \ln(1 - X_{Cl_2}^f) + \frac{(2N_1 + 3)^3 \cdot X_{Cl_2}^f}{(N_1 - 1)(1 - X_{Cl_2}^f)} - \frac{(3N_1 + 2)^3}{(N_1 - 1)^2} \ln\left(\frac{N_1 - X_{Cl_2}^f}{N_1}\right) \right\} \quad (46)$$

Then

$$X = k_1' \tau \quad (47)$$

A plot of X versus τ will give a straight line of slope k_1 or slope k_1' , as shown in Equations (44) and (47), if the correct rate expression has been chosen.

Rate and Design Equations Including Reverse Reaction

When the reaction reaches equilibrium, the rate of the forward reaction should equal the rate of the reverse reaction. If the forward reaction rate equation is set, the reverse reaction rate equation can be derived by using the equilibrium constant expression. Then the total reaction rate equation is the combination of the forward and reverse reaction rate equations.

For Reaction I,

$$K_{eq.} = \text{equilibrium constant} = \frac{k_1}{k_2} = \frac{[C_{HCl,eq.}]^2 [C_{O_2,eq.}]^{1/2}}{[C_{Cl_2,eq.}] [C_{H_2O,eq.}]}$$
(48)

For Reaction II,

$$K'_{eq.} = \text{equilibrium constant} = \frac{k'_1}{k'_2} = \frac{[C_{HCl,eq.}]^4 [C_{O_2,eq.}]}{[C_{Cl_2,eq.}]^2 [C_{H_2O,eq.}]^2}$$
(49)

1. If the forward reaction rate equation is

$$\text{Rate} = k_1 C_{Cl_2} \quad \text{or} \quad \text{Rate} = k'_1 C_{Cl_2} :$$

- a. For Reaction I

$$\text{Rate} = (-r_{Cl_2}) = k_1 \cdot C_{Cl_2} - k_2 \frac{C_{HCl}^2 C_{O_2}^{1/2}}{C_{H_2O}}$$
(50)

Combining Equations (11), (12), (13), (14) and (50) gives

$$\begin{aligned}
 (-r_{\text{Cl}_2}) &= k_1 \cdot \frac{2C_{\text{Cl}_2}^{\circ} (N_1 + 1)(1 - X_{\text{Cl}_2})}{2(N_1 + 1) + X_{\text{Cl}_2}} \\
 &- k_2 \cdot \frac{\frac{4C_{\text{Cl}_2}^{\circ} (N_1 + 1)X_{\text{Cl}_2}}{[2(N_1 + 1) + X_{\text{Cl}_2}]^2} \left[\frac{C_{\text{Cl}_2}^{\circ} (N_1 + 1)X_{\text{Cl}_2}}{2(N_1 + 1) + X_{\text{Cl}_2}} \right]^{1/2}}{\frac{2C_{\text{Cl}_2}^{\circ} (N_1 + 1)(N_1 - X_{\text{Cl}_2})}{[2(N_1 + 1) + X_{\text{Cl}_2}]}} \quad (51)
 \end{aligned}$$

After rearranging and using Equation (48),

$$\begin{aligned}
 (-r_{\text{Cl}_2}) &= \frac{2k_1 C_{\text{Cl}_2}^{\circ} (N_1 + 1)}{2(N_1 + 1) + X_{\text{Cl}_2}} \\
 &\left\{ 1 - X_{\text{Cl}_2} - \frac{4[C_{\text{Cl}_2}^{\circ}]^{1/2} \cdot (N_1 + 1)^{1/2} \cdot X_{\text{Cl}_2}^{5/2}}{K_{\text{eq.}} [2(N_1 + 1) + X_{\text{Cl}_2}]^{1/2} \cdot (N_1 - X_{\text{Cl}_2})} \right\} \quad (52)
 \end{aligned}$$

Combining Equations (52) and (27), and rearranging

$$\begin{aligned}
 \tau &= \frac{1}{2k_1 (N_1 + 1)} \int_0^{X_{\text{Cl}_2}^f} [2(N_1 + 1) + X_{\text{Cl}_2}] \\
 &\left\{ 1 - X_{\text{Cl}_2} - \frac{4[C_{\text{Cl}_2}^{\circ}]^{1/2} \cdot (N_1 + 1)^{1/2} \cdot X_{\text{Cl}_2}^{5/2}}{K_{\text{eq.}} \cdot [2(N_1 + 1) + X_{\text{Cl}_2}]^{1/2} \cdot (N_1 - X_{\text{Cl}_2})} \right\}^{-1} dX_{\text{Cl}_2} \quad (53)
 \end{aligned}$$

Let
$$X = \frac{1}{2(N_1 + 1)} \int_0^{X_{\text{Cl}_2}^f} [2(N_1 + 1) + X_{\text{Cl}_2}]$$

$$\left\{ 1 - X_{Cl_2} - \frac{4[C_{Cl_2}^O]^{1/2} \cdot (N_1 + 1)^{1/2} \cdot X_{Cl_2}^{5/2}}{K_{eq.} \cdot [2(N_1 + 1) + X_{Cl_2}]^{1/2} \cdot (N_1 - X_{Cl_2})} \right\}^{-1} dX_{Cl_2} \quad (54)$$

Then

$$X = k_1 \tau \quad (55)$$

b. For Reaction II

$$\text{Rate} = (-r_{Cl_2}) = k_1' \cdot C_{Cl_2} - k_2' \frac{C_{HCl}^4 \cdot C_{O_2}}{C_{Cl_2} \cdot C_{H_2O}^2} \quad (56)$$

Combining Equations (11), (12), (13), (14) and (56) gives

$$\begin{aligned} (-r_{Cl_2}) &= k_1' \cdot \frac{2C_{Cl_2}^O (N_1 + 1)(1 - X_{Cl_2})}{2(N_1 + 1) + X_{Cl_2}} \\ &\quad - k_2' \cdot \frac{\left[\frac{4C_{Cl_2}^O (N_1 + 1)X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} \right]^4 \left[\frac{C_{Cl_2}^O (N_1 + 1)X_{Cl_2}}{2(N_1 + 1) + X_{Cl_2}} \right]}{\left[\frac{2C_{Cl_2}^O (N_1 + 1)(1 - X_{Cl_2})}{2(N_1 + 1) + X_{Cl_2}} \right] \left[\frac{2C_{Cl_2}^O (N_1 + 1)(N_1 - X_{Cl_2})}{2(N_1 + 1) + X_{Cl_2}} \right]^2} \end{aligned} \quad (57)$$

After rearranging and using Equation (49),

$$\begin{aligned} (-r_{Cl_2}) &= \frac{2k_1' C_{Cl_2}^O (N_1 + 1)}{2(N_1 + 1) + X_{Cl_2}} \\ &\quad \left\{ 1 - X_{Cl_2} - \frac{16 \cdot C_{Cl_2}^O (N_1 + 1)X_{Cl_2}^5}{K_{eq.} \cdot (N_1 - X_{Cl_2})^2 \cdot (1 - X_{Cl_2}) [2(N_1 + 1) + X_{Cl_2}]} \right\} \end{aligned} \quad (58)$$

Combining Equations (27) and (58), and rearranging

$$\tau = \frac{1}{2k'_1(N_1 + 1)} \int_0^{x_{Cl_2}^f} [2(N_1 + 1) + x_{Cl_2}] \left\{ 1 - x_{Cl_2} - \frac{16 \cdot c_{Cl_2}^0 (N_1 + 1) x_{Cl_2}^5}{K'_{eq.} \cdot (N_1 - x_{Cl_2})^2 (1 - x_{Cl_2}) [2(N_1 + 1) + x_{Cl_2}]} \right\}^{-1} dx_{Cl_2} \quad (59)$$

Let

$$X = \frac{1}{2(N_1 + 1)} \int_0^{x_{Cl_2}^f} [2(N_1 + 1) + x_{Cl_2}] \left\{ 1 - x_{Cl_2} - \frac{16 \cdot c_{Cl_2}^0 (N_1 + 1) x_{Cl_2}^5}{K'_{eq.} \cdot (N_1 - x_{Cl_2})^2 \cdot (1 - x_{Cl_2}) [2(N_1 + 1) + x_{Cl_2}]} \right\}^{-1} dx_{Cl_2} \quad (60)$$

Then

$$X = k' \tau \quad (61)$$

2. If the forward reaction rate equation is

$$\begin{aligned} \text{Rate} &= k'_1 c_{Cl_2}^2 c_{H_2O} \\ \text{Rate} &= (-r_{Cl_2}) = k'_1 c_{Cl_2}^2 c_{H_2O} - \frac{c_{HCl}^4 c_{O_2}}{c_{H_2O}} \end{aligned} \quad (62)$$

Combining Equations (11), (12), (13), (14), and (62) gives

$$(-r_{Cl_2}) = k'_1 \cdot \left[\frac{2c_{Cl_2}^0 (N_1 + 1) (1 - x_{Cl_2})}{2(N_1 + 1) + x_{Cl_2}} \right]^2 \left[\frac{2c_{Cl_2}^0 (N_1 + 1) (N_1 - x_{Cl_2})}{2(N_1 + 1) + x_{Cl_2}} \right]$$

$$- k'_2 \cdot \frac{\frac{4C_{Cl_2}^0 (N_1 + 1) X_{Cl_2}}{[2(N_1 + 1) + X_{Cl_2}]}^4 \left[\frac{C_{Cl_2}^0 (N_1 + 1) X_{Cl_2}}{[2(N_1 + 1) + X_{Cl_2}]} \right]}{\frac{2C_{Cl_2}^0 (N_1 + 1) (N_1 - X_{Cl_2})}{[2(N_1 + 1) + X_{Cl_2}]}} \quad (63)$$

After rearranging and using Equation (49),

$$(-r_{Cl_2}) = \frac{8k'_1 [C_{Cl_2}^0]^3 (N_1 + 1)^3}{[2(N_1 + 1) + X_{Cl_2}]^3} \left\{ (1 - X_{Cl_2})^2 (N_1 - X_{Cl_2}) \right. \\ \left. - \frac{16 \cdot C_{Cl_2}^0 (N_1 + 1) X_{Cl_2}^5}{K'_{eq.} \cdot (N_1 - X_{Cl_2}) \cdot [2(N_1 + 1) + X_{Cl_2}]} \right\} \quad (64)$$

Combining Equations (27) and (64) and rearranging

$$\tau = \frac{1}{8k'_1 \cdot [C_{Cl_2}^0]^2 \cdot (N_1 + 1)^3} \int_0^{X_{Cl_2}^f} [2(N_1 + 1) + X_{Cl_2}]^3 \\ \left\{ (1 - X_{Cl_2})^2 (N_1 - X_{Cl_2}) - \frac{16 \cdot C_{Cl_2}^0 \cdot (N_1 + 1) \cdot X_{Cl_2}^5}{K'_{eq.} \cdot (N_1 - X_{Cl_2}) \cdot [2(N_1 + 1) + X_{Cl_2}]} \right\}^{-1} \\ dX_{Cl_2} \quad (65)$$

Let

$$X = \frac{1}{8 \cdot [C_{Cl_2}^0]^2 \cdot (N_1 + 1)^3} \int_0^{X_{Cl_2}^f} [2(N_1 + 1) + X_{Cl_2}]^3 \cdot \\ \left\{ (1 - X_{Cl_2})^2 (N_1 - X_{Cl_2}) - \frac{16 \cdot C_{Cl_2}^0 \cdot (N_1 + 1) \cdot X_{Cl_2}^5}{K'_{eq.} \cdot (N_1 - X_{Cl_2}) \cdot [2(N_1 + 1) + X_{Cl_2}]} \right\}^{-1} dX_{Cl_2} \quad (66)$$

Then

$$X = k_1' \tau \quad (67)$$

A plot of X versus τ will give a straight line of slope k_1 or slope k_1' as shown in Equations (55), (61), and (67), if the correct rate expression has been chosen. The value of X in Equations (54), (60), and (66) can only be obtained by using a numerical integration method. Simpson's method was used in those cases.

The Values of $K_{eq.}$ and $K'_{eq.}$

The values of $K_{eq.}$ and $K'_{eq.}$ at both 900 and 950°K should be available for calculating the values of X in Equations (55), (61), and (67). The equilibrium constant (based on activities) of the Deacon reaction is expressed as a function of temperature in Equation (1). A sign-change for the right-hand side terms of Equation (1) yields Equation (68), in which the equilibrium constant of the reverse Deacon reaction (Reaction II) is expressed as a function of temperature.

$$\begin{aligned} \log K' = & - \frac{4881.7}{T} + 0.93035 \log T - (1.3704 \times 10^{-4})T \\ & + (1.7581 \times 10^{-8})T^2 + 4.1744 \end{aligned} \quad (68)$$

$$K' = \frac{(a_{HCl})^4 (a_{O_2})}{(a_{Cl_2})^2 (a_{H_2O})^2} \quad (69)$$

$$\left. \begin{aligned} a_{\text{Cl}_2} &= M_{\text{Cl}_2} \cdot v_{\text{Cl}_2} \cdot P_t \\ a_{\text{H}_2\text{O}} &= M_{\text{H}_2\text{O}} \cdot v_{\text{H}_2\text{O}} \cdot P_t \\ a_{\text{HCl}} &= M_{\text{HCl}} \cdot v_{\text{HCl}} \cdot P_t \\ a_{\text{O}_2} &= M_{\text{O}_2} \cdot v_{\text{O}_2} \cdot P_t \end{aligned} \right\} \quad (70)$$

At atmospheric pressure the fugacity coefficients for all gases are close to unity. And $P_t = 1 \text{ atm.}$, so Equation (70) becomes

$$\left. \begin{aligned} a_{\text{Cl}_2} &= M_{\text{Cl}_2} = \frac{n_{\text{Cl}_2}}{n_t} \\ a_{\text{H}_2\text{O}} &= M_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_t} \\ a_{\text{HCl}} &= M_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_t} \\ a_{\text{O}_2} &= M_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_t} \end{aligned} \right\} \quad (71)$$

Combining Equations (69) and (71),

$$K' = \frac{\left(\frac{n_{\text{HCl}}}{n_t}\right)^4 \left(\frac{n_{\text{O}_2}}{n_t}\right)}{\left(\frac{n_{\text{Cl}_2}}{n_t}\right)^2 \left(\frac{n_{\text{H}_2\text{O}}}{n_t}\right)^2} = \frac{n_{\text{HCl}}^4 \cdot n_{\text{O}_2}}{n_{\text{Cl}_2}^2 \cdot n_{\text{H}_2\text{O}}^2} \cdot \frac{1}{n_t} \quad (72)$$

$$\left. \begin{aligned} \text{Because } C_{\text{Cl}_2, \text{eq.}} &= \frac{n_{\text{Cl}_2}}{V} \\ C_{\text{H}_2\text{O}, \text{eq.}} &= \frac{n_{\text{H}_2\text{O}}}{V} \\ C_{\text{HCl}, \text{eq.}} &= \frac{n_{\text{HCl}}}{V} \\ C_{\text{O}_2, \text{eq.}} &= \frac{n_{\text{O}_2}}{V} \end{aligned} \right\} \quad (73)$$

Equation (72) can be rearranged and combined with Equation (73)

$$K' = \frac{(C_{\text{HCl,eq.}})^4 (C_{\text{O}_2\text{,eq.}})}{(C_{\text{Cl}_2\text{,eq.}})^2 (C_{\text{H}_2\text{O,eq.}})^2} \cdot \frac{V}{n_t} \quad (74)$$

Combining Equations (49) and (74) gives

$$K'_{\text{eq.}} = K' \times \frac{n_t}{V} \quad (75)$$

1. For Reaction II

K' , calculated from Equation (68), equals 1.899 at 900°K and 4.356 at 950°K. Using the ideal gas law, n_t/V equals 0.01355 g-moles/l at 900°K and 0.1284 g-moles/l at 950°K. Therefore, $K'_{\text{eq.}}$, calculated from Equation (75), equals 0.0257 at 900°K and 0.0559 at 950°K.

2. For Reaction I

The equilibrium constant K , based on activity, can be expressed as

$$\frac{(a_{\text{HCl}})^2 \cdot (a_{\text{O}_2})^{1/2}}{a_{\text{Cl}_2} \cdot a_{\text{H}_2\text{O}}}.$$

By comparing this expression with Equation (69), the following equation can be derived.

$$K = (K')^{1/2} \quad (76)$$

Combining Equations (71) and (73) with the activity-based expression of K ,

$$\begin{aligned}
 K &= \frac{\left(\frac{n_{\text{HCl}}}{n_t}\right)^2 \left(\frac{n_{\text{O}_2}}{n_t}\right)^{1/2}}{\left(\frac{n_{\text{Cl}_2}}{n_t}\right) \left(\frac{n_{\text{H}_2\text{O}}}{n_t}\right)} = \frac{\left(\frac{n_{\text{HCl}}}{V}\right)^2 \cdot \left(\frac{n_{\text{O}_2}}{V}\right)^{1/2}}{\left(\frac{n_{\text{Cl}_2}}{V}\right) \left(\frac{n_{\text{H}_2\text{O}}}{V}\right)} \cdot \left(\frac{V}{n_t}\right)^{1/2} \\
 &= \frac{(C_{\text{HCl},\text{eq.}})^2 \cdot (C_{\text{O}_2,\text{eq.}})^{1/2}}{(C_{\text{Cl}_2,\text{eq.}})(C_{\text{H}_2\text{O},\text{eq.}})} \cdot \left(\frac{V}{n_t}\right)^{1/2} \quad (77)
 \end{aligned}$$

Combining Equations (48) and (77) gives

$$K_{\text{eq.}} = K \times \left(\frac{n_t}{V}\right)^{1/2} \quad (78)$$

K, calculated from Equation (76), equals 1.378 at 900°K and 2.087 at 950°K. $K_{\text{eq.}}$, calculated from Equation (78), equals 0.1604 at 900°K and 0.2365 at 950°K.

RESULTS AND DISCUSSION

The Results and Discussion of Five-Pass Reactor at 900 and 950°K

The experiments were run at atmospheric pressure and two temperatures, 900 and 950°K. The results are given in Tables 1 and 2. The theoretical equilibrium conversions are also listed in the table. Since the measured conversions are always less than 50% of the equilibrium conversions, the reverse reaction is considered negligible. Later, the results calculated by including the reverse reaction will be presented to show that the reverse reaction can actually be neglected.

Table 3 lists the twelve kinetic models which were tested for the forward reaction.

Appendix III explains why models G, H, and L are suggested.

Among the twelve models in Table 3, model B appears to give the best fit of the results. A plot of Equation (44) is shown in Figure 5 for both 900 and 950°K experiments. Table 4 lists the values of X calculated from Equation (43). The values of k_1 are 0.032 sec^{-1} at 900°K and 0.051 sec^{-1} at 950°K. Based on the Arrhenius relationship, $k = A \cdot \exp. (-E/RT)$, gives $A = \text{frequency factor} = 224 \text{ sec}^{-1}$ and $E = \text{activation energy} = 66.2 \text{ KJ/g-mole}$. (See Appendix IV.)

All twelve rate expressions were similarly analyzed. With one exception, model E, none of the other rate expressions approximated a linear relationship (e.g. Figures 6 and 7 of model C and Figures 8 and 9 of model L, Table 4 lists the values of X for these two models). A plot of Equation (47) is shown in Figure 10 for both 900 and 950°K experiments. Table 4 lists the values of X calculated from Equation (46).

Table 1. Experimental results of five-pass reactor at 900°K^a

Run number	$U_{Cl_2}^o$ ^b (cc/min.)	$U_{H_2O}^o$ ^b (cc/min.)	U^o ^b (cc/min.)	τ (sec)	$C_{Cl_2}^o \times 10^3$ (g-moles/l)
A1	364	483	847	2.41	5.823
A2	242	483	725	2.81	4.523
A3	364	483	847	2.41	5.823
A4	242	483	725	2.81	4.523
A5	266	284	550	3.71	6.559
A6	327	284	611	3.34	7.258
A7	266	284	550	3.71	6.559
A8	327	284	611	3.34	7.258
A9	364	416	780	2.62	6.327
A10	242	416	658	3.10	4.987
A11	364	416	780	2.62	6.327
A12	242	416	658	3.10	4.987
A13	155	308	463	4.41	4.523
A14	187	308	495	4.12	5.108
A15	224	308	532	3.84	5.691
A16	266	308	574	3.55	6.276
A17	328	308	636	3.21	6.976
A18	242	308	550	3.71	5.958
A19	155	316	471	4.33	4.450
A20	187	316	503	4.06	5.030
A21	223	316	539	3.78	5.610
A22	266	316	582	3.50	6.193
A23	327	316	643	3.17	6.893
A24	155	158	313	6.52	6.695
A25	187	158	345	5.92	7.333
A26	224	158	382	5.35	7.931
A27	266	158	424	4.81	8.498
A28	328	158	486	4.20	9.135

^aDetailed calculations are shown in Appendix II.^bThe rates are based on 900°K.

Table 1. Continued

Run number	$C_{H_2O}^o \times 10^3$ (g-moles/l)	$U_{O_2}^c$ (cc/min.)	N_1	$x_{Cl_2}^f$ (%)	$(x_{Cl_2,eq.}^f)$ (%)
A1	7.727	4.12	1.327	6.91	57.50
A2	9.027	3.12	1.996	7.88	68.00
A3	7.727	4.12	1.327	6.91	57.50
A4	9.027	2.80	1.976	7.06	68.00
A5	6.991	4.05	1.066	9.24	52.00
A6	6.292	4.38	0.867	8.16	47.00
A7	6.991	4.05	1.066	9.24	52.00
A8	6.292	4.40	0.867	8.20	47.00
A9	7.223	4.98	1.141	8.34	53.50
A10	8.563	4.27	1.717	10.77	64.00
A11	7.223	4.96	1.141	8.31	53.50
A12	8.563	4.20	1.717	10.59	64.00
A13	9.028	3.50	1.996	13.82	68.00
A14	8.442	4.37	1.653	14.29	63.00
A15	7.859	5.17	1.381	14.13	58.50
A16	7.274	5.93	1.159	13.60	54.00
A17	6.574	6.47	0.942	12.06	50.00
A18	7.592	5.40	1.274	13.62	56.50
A19	9.102	2.40	2.046	9.48	68.50
A20	8.520	3.63	1.694	11.87	63.50
A21	7.941	4.10	1.416	11.20	59.00
A22	7.357	5.40	1.188	12.38	55.00
A23	6.657	5.80	0.966	10.81	49.50
A24	6.855	4.43	1.024	17.50	51.00
A25	6.217	5.17	0.848	16.90	46.00
A26	5.619	5.40	0.708	14.76	42.00
A27	5.052	5.87	0.594	13.46	38.00
A28	4.415	6.50	0.483	12.12	33.00

^cThe rates are based on 295°K.

Table 2. Experimental results of five-pass reactor at 950°K^a

Run number	$U_{Cl_2}^o$ ^b (cc/min.)	$U_{H_2O}^o$ ^b (cc/min.)	U^{ob} (cc/min.)	τ (sec)	$C_{Cl_2}^o \times 10^3$ (g-moles/l)
B1	164	168	332	6.14	6.365
B2	196	168	364	5.60	6.938
B3	235	168	403	5.06	7.505
B4	280	168	448	4.55	8.043
B5	345	168	513	3.98	9.127
B6	165	233	398	5.13	5.317
B7	197	233	430	4.74	5.882
B8	236	233	469	4.35	6.457
B9	281	233	514	3.97	7.018
B10	346	233	579	3.52	7.668
B11	164	277	441	4.62	4.792
B12	197	277	474	4.31	5.341
B13	235	277	512	3.98	5.908
B14	281	277	558	3.66	6.470
B15	345	277	622	3.28	7.132
B16	165	314	479	4.26	4.412
B17	198	314	512	3.99	4.944
B18	236	314	450	3.71	5.500
B19	282	314	596	3.42	6.058
B20	346	314	660	3.09	6.721

^aDetailed calculations are shown in Appendix II.^bThe rates are based on 950°K.

Table 2. Continued

Run number	$C_{H_2O}^o \times 10^3$ (g-moles/l)	$U_{O_2}^c$ (cc/min.)	N_1	$X_{Cl_2}^f$ (%)	$(X_{Cl_2}^f, eq.)$ (%)
B1	6.472	5.60	1.017	21.96	55.50
B2	5.898	7.10	0.850	23.28	57.50
B3	5.332	8.76	0.710	24.00	53.00
B4	4.794	10.07	0.596	23.15	46.00
B5	4.423	11.50	0.485	21.50	40.00
B6	7.520	5.00	1.414	19.61	73.50
B7	6.955	6.20	1.182	20.33	68.00
B8	6.380	7.50	0.988	20.55	62.50
B9	5.819	8.80	0.829	20.23	56.50
B10	5.169	9.60	0.674	17.94	50.00
B11	8.044	4.77	1.678	18.69	77.50
B12	7.496	6.17	1.403	20.22	73.00
B13	6.928	6.77	1.173	18.54	67.50
B14	6.366	7.50	0.984	17.24	62.50
B15	5.705	8.37	0.800	15.64	55.50
B16	8.424	5.07	1.909	19.87	81.00
B17	7.892	6.07	1.596	19.89	76.00
B18	7.336	7.03	1.334	19.27	72.00
B19	6.779	8.07	1.119	18.54	66.00
B20	6.116	8.63	0.910	16.14	60.00

^cThe rates are based on 295°K.

Table 3. Kinetic models

Model	Forward reaction rate expression
A	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}C_{\text{H}_2\text{O}}$
B	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}$
C	$(-r_{\text{Cl}_2}) = kC_{\text{H}_2\text{O}}$
D	$(-r_{\text{Cl}_2}) = k$
E	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}^2C_{\text{H}_2\text{O}}$
F	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}C_{\text{H}_2\text{O}}^2$
G	$(-r_{\text{Cl}_2}) = k \frac{C_{\text{Cl}_2}C_{\text{H}_2\text{O}}}{C_{\text{HCl}}}$
H	$(-r_{\text{Cl}_2}) = k \frac{C_{\text{Cl}_2}^2C_{\text{H}_2\text{O}}^2}{C_{\text{HCl}}^2}$
I	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}^2C_{\text{H}_2\text{O}}^2$
J	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}^2$
K	$(-r_{\text{Cl}_2}) = kC_{\text{H}_2\text{O}}^2$
L	$(-r_{\text{Cl}_2}) = kC_{\text{Cl}_2}^{1/2}C_{\text{H}_2\text{O}}$

Figure 5. X as a function of space-time for model B (five-pass reactor)

Table 4. Values of X

Run number	Equation (43)	Equation (54)	Equation (60)	Equation (46)	Equation (66)	Model C ^a	Model L ^b
A1	0.0721	0.0721	0.0722	1736	1710	0.0539	2.041
A2	0.0826	0.0826	0.0826	2182	2152	0.0406	1.746
A3	0.0721	0.0721	0.0722	1736	1710	0.0539	2.041
A4	0.0736	0.0736	0.0737	1930	1902	0.0362	1.556
A5	0.0980	0.0980	0.0982	2409	2377	0.0917	3.300
A6	0.0861	0.0861	0.0862	2118	2089	0.0999	3.409
A7	0.0980	0.0980	0.0982	2918	2377	0.0917	3.300
A8	0.0865	0.0865	0.0866	2129	2101	0.1005	3.427
A9	0.0879	0.0879	0.0880	2132	2106	0.0766	2.800
A10	0.1151	0.1151	0.1152	3011	2975	0.0654	2.710
A11	0.0876	0.0876	0.0877	2124	2097	0.0764	2.789
A12	0.1130	0.1130	0.1131	2951	2916	0.0643	2.661
A13	0.1505	0.1505	0.1507	4235	4177	0.0726	3.187
A14	0.1563	0.1563	0.1567	4228	4178	0.0916	3.796
A15	0.1546	0.1546	0.1551	4081	4032	0.1096	4.301
A16	0.1485	0.1485	0.1490	3816	3822	0.1268	4.736
A17	0.1306	0.1306	0.1309	3369	3332	0.1392	4.907
A18	0.1486	0.1486	0.1490	3876	3832	0.1148	4.398
A19	0.1004	0.1004	0.1004	2714	2678	0.0478	2.087
A20	0.1278	0.1278	0.1279	3378	3335	0.0735	3.041

$$a_X = \frac{-x_{Cl_2}^f - (3N_1 + 2)\ln((N_1 - x_{Cl_2}^f)/N_1)}{2(N_1 + 1)}$$

$$b_X = \left\{ \int_0^{x_{Cl_2}^f} \left[2(N_1 + 1) + x_{Cl_2} \right]^{3/2} / ((1 - x_{Cl_2})^{1/2} (N_1 - x_{Cl_2})) dx_{Cl_2} \right\} / [(C_{Cl_2}^o)^{1/2} \cdot (N_1 + 1)^{3/2}]$$

Table 4. Continued

Run number	Equation (43)	Equation (54)	Equation (60)	Equation (46)	Equation (66)	Model C ^a	Model L ^b
A21	0.1202	0.1202	0.1203	3062	3024	0.0834	3.263
A22	0.1341	0.1341	0.1344	3438	3391	0.1116	4.178
A23	0.1160	0.1160	0.1162	2934	2895	0.1203	4.250
A24	0.1967	0.1967	0.1981	5480	5413	0.1916	7.032
A25	0.1895	0.1895	0.1911	5402	5340	0.2275	7.974
A26	0.1632	0.1633	0.1645	4708	4656	0.2390	7.999
A27	0.1477	0.1477	0.1488	4429	4383	0.2626	8.457
A28	0.1319	0.1319	0.1329	4241	4190	0.2951	9.129
B1	0.2550	0.2550	0.2574	8511	8430	0.2502	9.582
B2	0.2737	0.2738	0.2779	9779	9695	0.3306	12.224
B3	0.2845	0.2848	0.2909	11078	11000	0.4280	15.300
B4	0.2733	0.2736	0.2806	11456	11385	0.5110	17.626
B5	0.2512	0.2516	0.2589	10405	10347	0.6090	19.634
B6	0.2229	0.2229	0.2238	7058	6982	0.1524	6.311
B7	0.2328	0.2328	0.2342	7446	7370	0.1933	7.641
B8	0.2362	0.2362	0.2382	7740	7663	0.2394	9.059
B9	0.2325	0.2326	0.2349	7890	7816	0.2878	10.451
B10	0.2032	0.2032	0.2051	7085	7014	0.3182	10.972
B11	0.2106	0.2106	0.2112	6720	6645	0.1202	5.218
B12	0.2308	0.2308	0.2319	7369	7292	0.1590	6.584
B13	0.2096	0.2096	0.2106	6526	6456	0.1758	6.889
B14	0.1935	0.1935	0.1944	6005	5940	0.1969	7.348
B15	0.1739	0.1739	0.1747	5475	5415	0.2224	7.869
B16	0.2254	0.2254	0.2261	7481	7396	0.1118	5.076
B17	0.2262	0.2262	0.2270	7271	7193	0.1357	5.828
B18	0.2186	0.2186	0.2196	6874	6799	0.1593	6.481
B19	0.2097	0.2097	0.2108	6550	6480	0.1852	7.170
B20	0.1798	0.1798	0.1807	5552	5492	0.1995	7.278

Figure 6. X as a function of space-time for model C at 900°K (five-pass reactor)

Figure 7. X as a function of space-time for model C at 950°K (five-pass reactor)

Figure 8. X as a function of space-time for model L at 900°K (five-pass reactor)

Figure 9. X as a function of space-time for model L at 950°K (five-pass reactor)

Figure 10. X as a function of space-time for model E (five-pass reactor)

The straight lines yield the constants $k_1' = 980 \text{ (g-moles/l)}^{-2} \text{ sec}^{-1}$ at 900°K, $k_1' = 1760 \text{ (g-moles/l)}^{-2} \text{ sec}^{-1}$ at 950°K, $A = 6.6 \times 10^7 \text{ (g-moles/l)}^{-2} \text{ sec}^{-1}$, and $E = 83.24 \text{ KJ/g-mole}$.

Because the experimental data seem to fit only the two forward reaction rate expressions, models B and E, these two models were used to derive the combined forward and reverse reaction rate expressions (see Theory Section, p. 24). Table 4 lists the values of X calculated from Equations (54), (60), and (66) at 900 and 950°K. The assumption that the reverse reaction can be neglected can be easily justified by comparison of those values.

Model B can be justified mechanistically in that it implies that the reaction which forms chlorine radicals, $\text{Cl}_2 \rightleftharpoons 2\text{Cl}\cdot$, is rate controlling. The slightly greater dispersion of data at 950°K might suggest that the formation of chlorine radicals is not the only rate-controlling step at higher temperatures.

The dissociation of chlorine gas into chlorine radicals was found to occur in a few photochemical reactions (5, 13, 30). The Gibbs free energy for this reaction is 33.77 Kcals/g-mole at 900°K and 32.37 Kcals/g-mole at 950°K. And the equilibrium constant, $K = \frac{[\text{Cl}\cdot]^2}{[\text{Cl}_2]}$, is 6.3×10^{-9} at 900°K and 3.6×10^{-8} at 950°K (25).

If the activated-complex theory is applied, the elementary reaction for model B and model E can be expressed as $\text{Cl}_2 \longrightarrow (\text{Cl}_2^\ddagger) \longrightarrow \text{products}$ (Reaction III) and $2\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow (\text{Cl}_2 \cdot \text{H}_2\text{O} \cdot \text{Cl}_2^\ddagger) \longrightarrow \text{products}$ (Reaction IV). For Reactions III and IV, at 925°K, the Gibbs free energy of activation are 106.58 and 42.92 Kcals/g-mole, the enthalpy of activation are 14.00 and 14.38 Kcals/g-mole, and the

entropy of activation are - 51.90 cal/g-mole. $^{\circ}$ K and - 30.85 cal/g-mole. $^{\circ}$ K. Detailed calculations are shown below.

E_a = Arrhenius activation energy

$\Delta G^{\ddagger}$ = Gibbs free energy of activation

$\Delta H^{\ddagger}$ = enthalpy of activation

$\Delta S^{\ddagger}$ = entropy of activation

n = order of the reaction

k = Boltzmann constant = 1.30×10^{-16} erg./ $^{\circ}$ K

h = Planck constant = 6.624×10^{-27} erg. $\cdot$ sec.

T = absolute temperature

For model B:

$$k_1 = \frac{kT}{h} \cdot \exp.(-\Delta G^{\ddagger}/RT)$$

$$= \frac{kT}{h} \cdot \exp.(\Delta S^{\ddagger}/R) \cdot \exp.(-\Delta H^{\ddagger}/RT)$$

$$\begin{aligned}\Delta H^{\ddagger} &= E_a - nRT = 15.84 - 1.987 \times 925 \times 10^{-3} = 14.00 \text{ Kcal/g-mole} \\ &= 58.57 \text{ K.J./g-mole}\end{aligned}$$

$$k_1 = A \cdot \exp.(-E_a/RT)$$

$$= 224 \cdot \exp.(-15.84 \times 10^3/1.987 \times 925)$$

$$= 0.0405 \text{ (sec}^{-1}\text{)}$$

$$\begin{aligned}0.0405 &= \frac{1.3 \times 10^{-16} \cdot 925}{6.624 \times 10^{-27}} \cdot \exp.(\Delta S^{\ddagger}/R) \cdot \exp.(-14.00 \times 10^3/ \\ &\quad 1.987 \cdot 925)\end{aligned}$$

$$\Delta S^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = 58.57 - 925 \times (-0.0519)$$

$$= 106.58 \text{ Kcal/mole} = 446.14 \text{ K.J./g-mole}$$

For model E:

$$k_1' = \frac{kT}{h} \cdot \exp.(\Delta S^\ddagger/R) \cdot \exp.(-\Delta H^\ddagger/RT)$$

$$\Delta H^\ddagger = E_a - nRT = 19.89 - 3 \cdot 1.987 \cdot 925 \times 10^{-3}$$

$$= 14.38 \text{ Kcals/g-mole} = 60.18 \text{ K.J./g-mole}$$

$$k_1' = 6.6 \times 10^7 \cdot \exp.(-19.89 \times 10^3 / 1.987 \cdot 925)$$

$$= 1314.68 \text{ (g-moles/l)}^{-2} \cdot \text{sec}^{-1}$$

$$1314.68 = \frac{1.30 \times 10^{-16} \cdot 925}{6.624 \times 10^{-27}} \cdot \exp.(\Delta S^\ddagger/R) \cdot \exp.(-14.38 \times 10^3 / 1.987 \cdot 925)$$

$$\Delta S^\ddagger = -30.85 \text{ cal/g-mole} \cdot ^\circ\text{K} = -129.07 \text{ joules/g-mole} \cdot ^\circ\text{K}$$

$$\Delta G^\ddagger = 14.38 - 925 \cdot 0.03085 = 42.92 \text{ (Kcals/g-mole)}$$

$$= 179.65 \text{ (K.J./g-mole)}$$

Comparing these thermodynamic properties, the entropy of activation for model E seems to be more realistic than that for model B. However, model B, shown in Figure 5, appears to give a slightly better fit of the data than model E, shown in Figure 10.

The results achieved by using the current equipment cannot really prove that the radicals exist in the reverse Deacon reaction at 900 and 950°K. There are a few methods that can be used to help determine whether the reaction system contains radicals (30). Even if the

presence of radicals could be confirmed, there would exist many possible mechanisms for the reverse Deacon reaction. Just like the controversial mechanisms of many photochemical and thermal reactions, unless solid proof can be found, the reaction mechanism will remain undetermined. But, by using better designed equipment and by applying the statistical sensitivity analysis method, an experimental reaction rate expression can still be justified (3, 42).

The space-time required in those experiments suggests that a catalyst would be justified to increase the reaction rate in a commercial scale reactor operating at 900 and 950°K. The catalyst candidates, which must not melt and sublime at those specific temperatures, are extremely limited, however. Cooling of the product gaseous stream would probably be rapid enough to avoid a significant amount of the reverse reaction. But the energy loss of this highly irreversible cooling process should also be considered as a disadvantage of this system. If the reaction temperature is raised to 1100°K, for which the equilibrium conversion is 66.5% for equal-molal feed, catalysts may not be necessary. But the cooling process for avoiding the reverse reaction would be an engineering problem, because the temperature of the product gaseous stream needs to be lowered in a very short time.

KI solution was used to trap the unreacted chlorine most of the time. NaOH and $\text{Na}_2\text{S}_2\text{O}_3$ solutions were also tried as substitutes for KI solution. But the results were not satisfactory because of the following reasons:

The kinetics for the second reaction are not available. But the thermodynamic data shows the equilibrium really favors the right hand side. The resulting oxygen evolved might have caused the unsatisfactory results.

- b. H_2S was generated when $\text{Na}_2\text{S}_2\text{O}_3$ solution was used (56). The oxygen evolution rates were therefore not accurate because of the presence of H_2S .

The Results of One-Pass Reactor at 900°K and the Discussion of Deviations from Plug Flow Assumptions

The results are given in Table 5. Comparing the values of X calculated from Equations (43), (54), and (60) shows that the reverse reaction can be neglected for model B. The same conclusion can be made for model E by comparing the values of X calculated from Equations (46) and (60). Plots of Equations (44) and (47) are shown in Figures 11 and 12 respectively. Those nine data points in Figure 11 apparently can be put into three groups. Each group forms a straight line which passes through the origin. Figure 12, although not that obviously, also shows the same pattern. It is noticed that the group with the largest slope happens to be the group with the highest flow rates in both cases.

Table 5. Experimental results of one-pass reactor at 900°K^a

Run number	$U_{Cl_2}^o$ ^b (cc/min.)	$U_{H_2O}^o$ ^b (cc/min.)	U^o ^b (cc/min.)	τ (sec)	$C_{Cl_2}^o \times 10^3$ (g-moles/l)	$C_{H_2O}^o \times 10^3$ (g-moles/l)	$U_{O_2}^c$ (cc/min.)	N_1	$x_{Cl_2}^f$ (%)
C1	142	358	500	20.64	3.848	9.702	5.91	2.521	25.40
C2	99	358	457	28.84	2.935	10.615	5.07	3.616	31.25
C3	164	358	522	19.78	4.257	9.293	6.46	2.183	24.03
C4	164	39	203	50.92	10.947	2.603	3.47	0.238	12.91
C5	99	39	138	74.92	9.721	3.829	2.93	0.394	18.06
C6	142	39	181	57.04	10.630	29.20	3.23	0.275	13.88
C7	142	187	329	31.36	5.848	7.702	4.20	1.317	18.05
C8	99	187	286	36.10	4.690	8.860	3.71	1.889	22.86
C9	164	187	351	29.42	6.331	7.219	4.75	1.140	17.67

^aDetailed calculations are shown in Appendix II.

^bThe rates are based on 900°K.

^cThe rates are based on 295°K.

Table 5. Continued

Run number	Equation (43)	Equation (54)	Equation (60)	Equation (46)	Equation (66)
C1	0.2986	0.3004	0.2986	10262	10155
C2	0.3814	0.3839	0.3815	16257	16099
C3	0.2803	0.2820	0.2803	9066	8791
C4	0.1419	0.1460	0.1422	8367	8302
C5	0.2059	0.2134	0.2064	9047	8996
C6	0.1536	0.1580	0.1538	8085	8021
C7	0.2031	0.2042	0.2031	5631	5569
C8	0.2649	0.2667	0.2649	8161	8075
C9	0.1986	0.1999	0.1986	5489	5429

Figure 11. X as a function of space-time for model B at 900°K (one-pass reactor)

Figure 12. X as a function of space-time for model E at 900°K (one-pass reactor)

Table 6 lists the highest and the lowest Reynolds numbers at the reactor entrance. It shows that the flow patterns of all the experiments are laminar.

Table 6.^a

Run number	Reynolds No.	
	Highest	Lowest
A1	49.67	
A24		19.34
B20	37.35	
B1		19.13
C3	6.30	
C5		2.49

^aDetailed calculations are shown in Appendix VI.

According to Denbigh (17), transverse temperature gradients, transverse and longitudinal diffusion, and transverse velocity gradient cause deviations from plug flow.

The reverse Deacon reaction is endothermic at 900°K. The heat of reaction when one g-mole of steam reacts completely with one g-mole of chlorine is 14.223 Kcals. The conversion and the molal flow rates of both reactants are so low for those experiments that an isothermal reactor can be assumed without much error. Therefore, the transverse temperature gradient is not the cause for deviation from plug flow in this case.

Because the flow patterns are laminar, the diffusional mechanism which is operative is the ordinary molecular diffusion. The effect of molecular diffusion for gases reduces the influence of the velocity

distribution in causing a deviation from plug flow. However, this positive effect is offset by the effect of the longitudinal molecular diffusion which is determined mainly by the ratio of the length of reactor to its diameter. That ratio of the five-pass reactor is 210, which is fourteen times larger than the value of the one-pass reactor. That might be one of the reasons for the better performance of the five-pass reactor.

The existence of velocity gradients at right-angles to the direction of fluid flow is the third form of deviation from the plug flow. The fluid velocity is smaller in the vicinity of the wall than it is near the reactor center. Therefore, elements of fluid moving closer to the wall have a larger space-time and tend to react to a greater extent. Because the velocity profile of turbulent flow is much flatter than the velocity profile of laminar flow, it is obvious that the greatest deviation from the reactor performance estimated by using the plug flow assumptions occurs in the case of laminar flow. In actual practice the velocity gradient is usually a great deal less significant than the influences of transverse temperature gradients and transverse diffusion which have been discussed previously. Therefore, even though the flow patterns of those experiments are laminar, the deviation caused by the velocity gradients is considered negligible.

Besides the three causes mentioned above, the effect of imperfect mixing is considered to be very serious in causing the deviation. With higher Reynolds numbers the mixing of the reactants should be better. Refer back to Figure 11, the group with the highest value of

k_1 is the group with the largest flow rates and this k_1 is less than half of the k_1 from five-pass reactor. The average Reynolds number for those experiments using the five-pass reactor is seven times larger than for the one-pass reactor.

Estimation of the Reactor Size

Conditions:

1. A 2000 MW reactor is used to drive a thermochemical water splitting reaction which is 50% efficient. Therefore, the available chemical energy in the hydrogen is 1000 MW.
2. The reverse Deacon reaction (Reaction I) is the oxygen-generation step. And Equation (50) is its reaction rate expression.

The heat of dissociation of one g-mole of liquid water at 298.15°K is 68.32 Kcals. The theoretical molal production rate of hydrogen is 1.26×10^7 g-moles/hr $\left(\frac{2 \times 10^6 \text{ KW} \times 50\% \times 8.6 \times 10^2 \text{ Kcals/hr}}{68.32 \text{ Kcals/g-mole}} \right)$. The theoretical molal production rate of oxygen, which is half of the rate of hydrogen, is 6.3×10^6 g-moles/hr. For Reaction I with $N_1 = 1$ at 900°K and 50 atms, the equilibrium constant, K_{eq} , is 0.1604 and the equilibrium conversion, $x_{Cl_2,eq}^f$, is 30%. The initial concentration of chlorine, $C_{Cl_2}^o$, is 0.339 g-moles/l (by applying the ideal gas law).

Equation (53) becomes

$$\tau = 7.81 \int_0^{x_{Cl_2}^f} (4 + x_{Cl_2}) \left\{ 1 - x_{Cl_2} - \frac{20.53 x_{Cl_2}^{5/2}}{(4 + x_{Cl_2})^{1/2} (1 - x_{Cl_2})} \right\}^{-1} dx_{Cl_2} \quad (79)$$

If the final conversion based on chlorine is 30%, which is 100% of the equilibrium conversion, the space-time in Equation (79) will be 135.33 seconds and the total flow rate entering the reactor will be 8.4×10^7 g-moles/hr (1.24×10^8 l/hr). Therefore the reactor volume, which is the product of the space-time and the total flow rate, is 4660 m^3 .

If the final conversion is 24%, which is 80% of the equilibrium conversion, the space-time will be 9.57 seconds and the flow rate will be 1.05×10^8 g-moles/l (1.55×10^8 l/hr). Then the reactor volume is 412 m^3 which is only one-eleventh of the volume for 100% of equilibrium.

If the value of N_1 is increased from 1 to 20, the equilibrium conversion is increased from 30% to 88.1%. Equation (53) becomes

$$\tau = 0.744 \int_0^{x_{Cl_2}^f} [42 + x_{Cl_2}] \left\{ 1 - x_{Cl_2} - \frac{20.53 x_{Cl_2}^{5/2}}{(42 + x_{Cl_2})^{1/2} (20 - x_{Cl_2})} \right\}^{-1} dx_{Cl_2} \quad (80)$$

If the conversion is 70% which is 80% of the equilibrium conversion, the space-time in Equation (80) will be 38.31 seconds and the total feed rate will be 3.78×10^8 g-moles/hr (5.58×10^8 l/hr). The reactor volume is 5940 m^3 which is fourteen times the volume for equal-molal feed with 24% conversion.

If the conversion is 80% which is almost 91% of the equilibrium conversion, the space-time will be 56.33 seconds and the total flow rate will be 3.31×10^8 g-moles/hr (4.88×10^8 l/hr). Therefore the

reactor volume is 7640 m^3 which is eighteen times of the volume for equal-molal feed with 24% conversion.

The increase of the value of N_1 will yield higher equilibrium conversion but also higher total flow rate and longer space-time. Therefore a larger size of reactor will be needed.

If the reactor temperature is raised to 950°K , the equilibrium constant, K_{eq} , is 0.2365 and the equilibrium conversion, $X_{\text{Cl}_2}^f$, is 34%. With $N_1 = 1$ Equation (53) becomes

$$\tau = 4.9 \int_0^{X_{\text{Cl}_2}^f} (4 + X_{\text{Cl}_2}) \left\{ 1 - X_{\text{Cl}_2} - \frac{13.55 X_{\text{Cl}_2}^{5/2}}{(4 + X_{\text{Cl}_2})^{1/2} (1 - X_{\text{Cl}_2})} \right\}^{-1} dX_{\text{Cl}_2} \quad (81)$$

If the final conversion is 24% which is 70% of the equilibrium conversion, the space-time in Equation (81) will be 5.61 seconds and the total feed rate will be 1.05×10^8 g-moles/hr (1.64×10^8 l/hr). The reactor volume is 256 m^3 which is 0.62 times of the volume for the case of 900°K , 50 atm, and 24% conversion.

The increase of the reaction temperature yields a more reasonable reactor volume. The available data is not accurate enough to show what the reactor size will be if the reaction temperature is raised to 1000°K or even 1100°K . But one thing can be sure, further reduction of the reactor size will be necessary to make this process successful. And that can be achieved either by raising the reactor temperature or by applying a suitable catalyst to the reaction.

RECOMMENDATION

There were no parameters other than the oxygen evolution rate to double-check the values of the reaction conversion for these experiments. A total material balance around the system was not obtained. In order to achieve more precise results, two methods which can be used to detect the concentration of each species in the gaseous product stream are suggested. One method is to use a gas chromatograph to analyze the samples taken from the exit of the reactor. The samples have to be quenched to stop both forward and reverse reactions. If the temperature is quenched below 100°C, the steam will condense and absorb some hydrogen chloride and chlorine. Then an accurate analytic method, which will be able to detect the precise amount of water, hydrogen chloride, and chlorine present in the liquid phase, has to be developed. If the reaction is quenched above 100°C so that the steam will not condense, the samples can be directly injected into the gas chromatograph which is also run at about 100°C. The other method is to use a spectrophotometer at the exit of the reactor to photometrically measure the concentration of certain species at a certain wave length (45, 46). The unchanged concentration reading will mean the system has already reached the steady state. Then a new wave length is set to get the concentration of another species.

The chlorine rotameter was calibrated at 5 psi by the manufacturer. The current chlorine regulator delivery pressure range of 4-100 psi is not precise enough to control the pressure at 5 psi. The inaccuracy of the pressure will affect the chlorine flow rates, and therefore

the values of the space-time, the conversion based on the chlorine flow rate, and the molal feed ratio. This problem can be solved by installing a line regulator with delivery pressure range of 0.5-8 psi or changing the original regulator to a corrosion-resistance regulator with delivery pressure range of 4-35 psi.

Thorough mixing is among the plug flow assumptions made for this system. Therefore, a nozzle type of mixing zone, which will increase the velocity of the gaseous mixture drastically, will be an ideal device to ensure perfect mixing.

Catalyst might be necessary for the reverse Deacon reaction to be economically feasible. A vertical reactor will be better to use as a catalytic system than a horizontal one.

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ACKNOWLEDGMENT

The author would like to express deep appreciation to Dr. Dean L. Ulrichson for his guidance and helpful suggestions throughout this study and in preparation of this manuscript.

Gratitude is also due Mr. Mike Murtha for his help in calculating the final results and for his constant consultation.

APPENDIX I. PARTIAL LISTING OF THERMOCHEMICAL CYCLES
WHICH USE THE REVERSE DEACON REACTION

1. DeBeni, Mark 3 (18)

	Temperature, °K
$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	1073
$2\text{HCl} + 2\text{VOCl} \longrightarrow 2\text{VOCl}_2 + \text{H}_2$	443
$4\text{VOCl}_2 \longrightarrow 2\text{VOCl} + 2\text{VOCl}_3$	873
$2\text{VOCl}_3 \longrightarrow 2\text{VOCl}_2 + \text{Cl}_2$	473

2. Hardy, Mark 4 (18)

	Temperature, °K
$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	1073
$2\text{HCl} + \text{S} + 2\text{FeCl}_2 \longrightarrow \text{H}_2\text{S} + 2\text{FeCl}_3$	373
$\text{H}_2\text{S} \longrightarrow \text{H}_2 + \frac{1}{2} \text{S}_2$	1073
$2\text{FeCl}_3 \longrightarrow 2\text{FeCl}_2 + \text{Cl}_2$	693

3. Hardy, Mark 7 (18)

	Temperature, °K
$3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	923
$\text{Fe}_3\text{O}_4 + \frac{1}{4} \text{O}_2 \longrightarrow \frac{3}{2} \text{Fe}_2\text{O}_3$	623
$\frac{3}{2} \text{Fe}_2\text{O}_3 + 9\text{HCl} \longrightarrow 3\text{FeCl}_3 + \frac{9}{2} \text{H}_2\text{O}$	423
$3\text{FeCl}_3 \longrightarrow 3\text{FeCl}_2 + \frac{3}{2} \text{Cl}_2$	693
$\frac{3}{2} \text{H}_2\text{O} + \frac{3}{2} \text{Cl}_2 \longrightarrow 3\text{HCl} + \frac{3}{2} \text{O}_2$	1073

4. DeBeni, Euratom (18)

	Temperature, °K
$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	1073
$2\text{HCl} + 2\text{CrCl}_2 \longrightarrow 2\text{CrCl}_3 + \text{H}_2$	443

5. Funk and Reinstrom, Vanadium Chloride Process (24)

Temperature, °K

6. Knoche, Cremer, and Steinborn, Iron Chloride Process (35)

Temperature, °K

7. Knoche, Chromium Chloride Process (9)

Temperature, °K

8. Copper Chloride Process (9)

Temperature, °K

9. HCl Thermal Decomposition Process (9)

Temperature, °K

973

1073

APPENDIX II. EXAMPLE OF CALCULATIONS

For run No. A1:

weight of steam generator before experiment = 1773.1 gm

weight of steam generator after experiment = 1741.8 gm

operating time for steam valve = 265.5 min.

mass flow rate of steam = $\frac{1773.1 - 1741.8}{265.5} = 0.118$ (gm/min.)

volumetric flow rate of steam at 900°K = $\frac{0.118}{18} \times 0.082 \times 900 = 483$ (cc/min.)

average oxygen evolution rate at 22°C (room temperature) =

4.125 cc/min.

reactor volume = 34 cc

volumetric flow rate of chlorine at 900°K = 364 cc/min.

τ = space-time = $\frac{34}{364 + 483} = 0.040$ (min.) = 2.41 (sec)

$X_{Cl_2}^f$ = conversion based on chlorine = $\frac{4.125 \times 2}{364 \times \frac{295}{900}} = 6.91\%$

assume steam and chlorine are ideal gases at 900°K:

$$C = \text{concentration} = \frac{n}{V} = \frac{\text{No. of moles}}{\text{volume}} = \frac{P}{RT} = \frac{\text{pressure}}{\text{gas constant} \times \text{temperature}}$$

The total pressure for the system is 1 atm.

$$P_{Cl_2}^o = \text{initial partial pressure of chlorine} = 1 \times \frac{364}{364 + 483} = 0.430 \text{ (atm)}$$

$$P_{H_2O}^o = \text{initial partial pressure of steam} = 1 \times \frac{483}{364 + 483} = 0.570 \text{ (atm)}$$

$$C_{Cl_2}^o = \text{initial concentration of chlorine} = \frac{P_{Cl_2}^o}{RT} = \frac{0.430}{0.082 \times 900} = 0.0058232 \text{ (g-moles/l)}$$

$$C_{H_2O}^o = \text{initial concentration of steam} = \frac{P_{H_2O}^o}{RT} = \frac{0.570}{0.082 \times 900} \\ = 0.0072269 \text{ (g-moles/l)}$$

$$N_1 = \text{molal feed ratio of steam to chlorine} = \frac{C_{H_2O}^o}{C_{Cl_2}^o} = \frac{0.0072269}{0.0058232} = 1.327$$

calculation of equilibrium conversion:

$$K = 0.1604 = \frac{(C_{HCl,eq.})^2 \cdot (C_{O_2,eq.})^{1/2}}{(C_{Cl_2,eq.}) \cdot (C_{H_2O,eq.})}$$

Using Equations (11), (12), (13), and (14) and rearranging gives

$$[2(N_1 + 1) + X_{Cl_2,eq.}]^{1/2} \cdot (1 - X_{Cl_2,eq.})^{(N_1 - X_{Cl_2,eq.})} \\ = 2.903 X_{Cl_2,eq.}^{5/2}$$

Then solving by trial and error yields

$$X_{Cl_2,eq.} = 57.50\%$$

APPENDIX III. SUGGESTED REACTION MECHANISMS FOR
MODELS G, H, AND L

1. Model G

The following mechanism is suggested.

At steady state:

$$k_1 \cdot C_{\text{Cl}_2} = k_2 \cdot C_{\text{Cl}\cdot}^2$$

$$k_3 \cdot C_{\text{Cl}\cdot}^2 \cdot C_{\text{H}_2\text{O}} = k_4 \cdot C_{\text{HOCl}} C_{\text{HCl}}$$

So
$$C_{\text{HOCl}} = \frac{k_1 k_3}{k_2 k_4} \frac{C_{\text{Cl}_2} C_{\text{H}_2\text{O}}}{C_{\text{HCl}}}$$

Then
$$\begin{aligned} \text{rate} = (-r_{\text{HOCl}}) &= k_5 \cdot C_{\text{HOCl}} - k_6 \cdot C_{\text{HCl}} C_{\text{O}_2}^{1/2} = \frac{k_1 k_3 k_5}{k_2 k_4} \frac{C_{\text{Cl}_2} C_{\text{H}_2\text{O}}}{C_{\text{HCl}}} \\ &\quad - k_6 \cdot C_{\text{HCl}} C_{\text{O}_2}^{1/2} \end{aligned}$$

2. Model H

The following mechanisms are suggested.

At steady state:

$$k_1 \cdot C_{Cl_2}^2 = k_2 \cdot C_{Cl}^4$$

$$k_3 \cdot C_{Cl}^4 \cdot C_{H_2O}^2 = k_4 \cdot C_{HOCl}^2 \cdot C_{HCl}^2$$

So
$$C_{HOCl}^2 = \frac{k_1 k_3}{k_2 k_4} \cdot \frac{C_{Cl_2}^2 C_{H_2O}^2}{C_{HCl}^2}$$

Then
$$\text{rate} = (-r_{HOCl}) = k_5 \cdot C_{HOCl}^2 - k_6 \cdot C_{HCl}^2 C_{O_2} = \frac{k_1 k_3 k_5}{k_2 k_4} \frac{C_{Cl_2}^2 C_{H_2O}^2}{C_{HCl}^2} - k_6 \cdot C_{HCl}^2 C_{O_2}$$

At steady state:

$$k_1 \cdot C_{Cl_2}^2 \cdot C_{H_2O} = k_2 \cdot C_{HCl}^2 \cdot C_{Cl_2O}$$

So
$$C_{Cl_2O} = \frac{k_1}{k_2} \cdot \frac{C_{Cl_2}^2 C_{H_2O}}{C_{HCl}^2}$$

Then
$$\text{rate} = (-r_{Cl_2O}) = (-r_{H_2O}) = k_3 \cdot C_{Cl_2O} \cdot C_{H_2O} - k_4 C_{HCl}^2 \cdot C_{O_2}$$

$$= \frac{k_1 k_3}{k_2} \cdot \frac{C_{Cl_2}^2 C_{H_2O}^2}{C_{HCl}^2} - k_4 C_{HCl}^2 C_{O_2}$$

3. Model L

The following chain-reaction mechanisms are suggested.

At steady state:

$$k_1 \cdot C_{\text{Cl}_2} = k_2 C_{\text{Cl}\cdot}^2$$

So $C_{\text{Cl}\cdot} = \left(\frac{k_1}{k_2}\right)^{1/2} C_{\text{Cl}_2}^{1/2}$

Then $\text{rate} = (-r_{\text{Cl}\cdot}) = (-r_{\text{H}_2\text{O}}) = k_3 C_{\text{Cl}\cdot} \cdot C_{\text{H}_2\text{O}} - k_4 C_{\text{HCl}} \cdot C_{\text{OH}\cdot}$

$$= \left[k_3 \cdot \left(\frac{k_1}{k_2}\right)^{1/2} \right] \cdot C_{\text{Cl}_2}^{1/2} C_{\text{H}_2\text{O}} - k_4 C_{\text{HCl}} \cdot C_{\text{OH}\cdot}$$

At steady state:

$$k_1 C_{\text{Cl}_2} = k_2 \cdot C_{\text{Cl}\cdot}^2$$

So $C_{\text{Cl}\cdot} = \left(\frac{k_1}{k_2}\right)^{1/2} \cdot C_{\text{Cl}_2}^{1/2}$

Then $\text{rate} = (-r_{\text{Cl}\cdot}) = (-r_{\text{H}_2\text{O}}) = k_3 C_{\text{Cl}\cdot} \cdot C_{\text{H}_2\text{O}} - k_4 \cdot C_{\text{HOCl}} \cdot C_{\text{H}\cdot}$

$$= \left[k_3 \cdot \left(\frac{k_1}{k_2}\right)^{1/2} \right] \cdot C_{\text{Cl}_2}^{1/2} C_{\text{H}_2\text{O}} - k_4 \cdot C_{\text{HOCl}} \cdot C_{\text{H}\cdot}$$

APPENDIX IV. CALCULATIONS OF FREQUENCY FACTOR AND
ACTIVATION ENERGY FOR MODEL B

Arrhenius equation

$$k = Ae^{-E/RT}$$

So $\ln k = \ln A - E/RT$

for model B

$$k_1 = 0.032 \text{ sec}^{-1} \text{ at } 900^\circ\text{K}$$

$$k_1 = 0.051 \text{ sec}^{-1} \text{ at } 950^\circ\text{K}$$

$$\left\{ \begin{array}{l} \ln 0.032 = \ln A - E/R \times 900 \text{ ————— (1)} \\ \ln 0.051 = \ln A - E/R \times 950 \text{ ————— (2)} \end{array} \right.$$

$$(2)-(1) \quad \ln \frac{0.051}{0.032} = \frac{50E}{R \times 900 \times 950}$$

$$E = 15.84 \text{ Kcal/g-mole} = 66.26 \text{ KJ/g-mole}$$

$$A = 224 \text{ sec}^{-1}$$

APPENDIX V. SUGGESTED REACTION MECHANISMS FOR MODEL B

The following mechanism is suggested to make the forward reaction rate expression fit the expression for model B.

At steady state:

$$k_3 \cdot \text{C}_{\text{Cl}\cdot}^2 \cdot \text{C}_{\text{H}_2\text{O}} = k_4 \cdot \text{C}_{\text{HOCl}} \cdot \text{C}_{\text{HCl}}$$

$$k_5 \cdot \text{C}_{\text{HOCl}} = k_6 \cdot \text{C}_{\text{HCl}} \cdot \text{C}_{\text{O}_2}^{1/2}$$

So
$$\text{C}_{\text{Cl}\cdot}^2 = \frac{k_4}{k_3} \cdot \frac{\text{C}_{\text{HOCl}} \cdot \text{C}_{\text{HCl}}}{\text{C}_{\text{H}_2\text{O}}} = \frac{k_4 k_6}{k_3 k_5} \cdot \frac{\text{C}_{\text{HCl}}^2 \text{C}_{\text{O}_2}^{1/2}}{\text{C}_{\text{H}_2\text{O}}}$$

Then
$$\text{rate} = k_1 \cdot \text{C}_{\text{Cl}_2} - k_2 \cdot \text{C}_{\text{Cl}\cdot}^2 = k_1 \cdot \text{C}_{\text{Cl}_2} - \frac{k_2 k_4 k_6}{k_3 k_5} \cdot \frac{\text{C}_{\text{HCl}}^2 \text{C}_{\text{O}_2}^{1/2}}{\text{C}_{\text{H}_2\text{O}}}$$

APPENDIX VI. EXAMPLE OF CALCULATIONS OF REYNOLDS NUMBER

Critical properties of steam and chlorine

steam: $T_c = 647^\circ\text{K}$, $P_c = 217.7$ atms, $\mu_c = 495$ micropoises

chlorine: $T_c = 417^\circ\text{K}$, $P_c = 76.1$ atms, $\mu_c = 420$ micropoises

for run No. A-1:

Mole-fraction of steam at the entrance of the reactor is $\frac{483}{847}$.

The following properties are of the reactant-mixture at the entrance of the reactor.

$$P_c^* = \text{critical pressure} = 217.7 \times \frac{483}{847} + 76.1 \times \frac{364}{847} = 156.8 \text{ (atms)}$$

$$T_c^* = \text{critical temperature} = 647 \times \frac{483}{847} + 417 \times \frac{364}{847} = 548 \text{ (}^\circ\text{K)}$$

$$\mu_c^* = \text{critical viscosity} = 495 \times \frac{483}{847} + 420 \times \frac{364}{847} = 463 \text{ (micropoises)}$$

$$P_r^* = \text{reduced pressure} = \frac{1}{156.8} = 0.0064$$

$$T_r^* = \text{reduced temperature} = \frac{900}{548} = 1.64$$

Then using Figure 175, Hougen's "Chemical Process Principle" P. 871

$$\mu_r^* = \text{reduced viscosity} = 0.72$$

$$\mu = \text{viscosity} = \mu_r^* \times \mu_c^* = 333 \text{ (micropoises)}$$

$$M = \text{molecular weight} = 18 \times \frac{483}{847} + 71 \times \frac{364}{847} = 40.78 \text{ (gms/g-mole)}$$

$$\rho = \text{density} = \frac{P \times M}{R \times T} = \frac{1 \times 40.78}{0.082 \times 900} = 0.55 \text{ (gms/l)}$$

$$\text{Reynolds No.} = \frac{4 \times U^o \times \rho}{\pi \times d \times \mu} = \frac{4 \times \frac{847}{60 \times 1000} \times 0.55}{\pi \times \frac{6}{10} \times 3.33 \times 10^{-4}} = 49.67$$