THERMOCHEMICAL WATER SPLITTING CYCLES:
OXYGEN LIBERATING REACTIONS

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M. S. Thesis Submitted To Iowa State University

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Date Transmitted: October 1975

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82

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24

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Thermochemical water splitting cycles: Oxygen liberating reactions

by

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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

1975

TABLE OF CONTENTS

	<u>Page</u>
NOMENCLATURE	vi
INTRODUCTION	1
Electrolysis	6
Thermochemical Cycles	8
Reverse Deacon Reaction and Alternatives	12
EXPERIMENTAL INVESTIGATION	18
Purpose	18
Analytical Techniques	26
Equipment and Procedures	30
Results and Discussion	34
Experimental Conclusions	51
THERMODYNAMICS AND PROCESS CALCULATIONS	52
Reverse Deacon Reaction	56
Magnesium Hydroxide Systems	62
Magnesium Oxide Reaction System	69
Other Reaction Systems	75
CONCLUSIONS AND RECOMMENDATIONS	76
BIBLIOGRAPHY	79
ACKNOWLEDGMENT	84
APPENDIX I. PARTIAL LISTING OF THERMOCHEMICAL CYCLES WHICH USE THE REVERSE DEACON REACTION	85
APPENDIX II. THERMOCHEMICAL CYCLES — EXAMPLES WHICH DO NOT EMPLOY REVERSE DEACON REACTION	88

APPENDIX III. COMBINED THERMOCHEMICAL-ELECTROLYTIC PROCESSES	90
APPENDIX IV. THERMODYNAMIC CONSTANTS	91
APPENDIX V. EXPERIMENTAL HISTORY	97

NOMENCLATURE

a	activity
H_f	enthalpy of formation
K	equilibrium constant
N	number of moles
n	number of components
P	total pressure
Q	an amount of heat absorbed at a high temperature
R	gas constant
S_f	entropy of formation
T	thermodynamic temperature
$T_{\min}$	minimum temperature at which heat is rejected (ambient)
$T_{\max}$	maximum temperature of the heat source
W_{sep}	separation work
X	mole fraction
ΔG	free energy change of reaction
ΔH	enthalpy change of reaction
ΔS	entropy change of reaction
η	efficiency of thermochemical cycles
ϕ	fugacity coefficient

INTRODUCTION

Many people in recent years have become aware of the pressure current energy demands are placing on our limited known sources of power. This issue, referred to by many as the "energy crisis," has spurred interest in assessing our total energy picture and investigating alternative sources of fuel.

Most of the global power presently consumed can be traced to energy from the sun stored primarily as coal, natural gas and petroleum. These three sources make up approximately 95% of the total energy use (Figure 1) (12). The only obvious alternatives to these limited energy sources are nuclear and solar power generation. Nuclear energy has emerged in the last two decades as an important source of power, while solar energy has only recently been seriously considered on a large scale. Both of these methods provide heat as the primary form of energy and most of the present day technology has concerned itself with production of electricity from large sources of heat. Presently, nuclear energy surfaces in the energy marketplace as electricity generated from heat produced by nuclear fission.

A recent study of the total energy usage, however, shows only about 20% (12) is used as electricity and thus present technology limits the impact nuclear energy can have on the marketplace (Figure 2).

The question of how nuclear power can be converted to a more flexible energy intermediate has generated widespread interest in a "hydrogen economy" (8, 13, 23, 30, 46, 47, 54), that is, the use of hydrogen as the fuel intermediate. Hydrogen is an attractive fuel for

Figure 1. Energy sources in the U.S. in 1970 (12).

Figure 2. Energy form consumed in the U.S. in 1970 (12).

a number of reasons, but primarily because of its minimal ecological impact. The main product from the combustion of hydrogen is water vapor, which can be discharged to the environment with little harmful effects. Since hydrogen can be produced from water by dissociation into the elements, its use as a fuel forms a natural cycle, with water being both the initial raw material and final waste of the cycle.

Introduction of an energy system based on hydrogen has been examined extensively in a report prepared for the American Gas Association by D. P. Gregory (21). This study written in 1973, discusses a variety of points including hydrogen production, transmission, storage, safety and finally hydrogen utilization. The conclusions drawn pointed out many advantages which a hydrogen economy possesses, but also stresses areas where continued research and development are necessary.

The two methods of hydrogen production most frequently discussed are electrolysis and thermochemical cycles. Both of these processes would use high temperature heat sources as the initial energy source, electricity, however, must be generated as an intermediate in the electrolysis process. These methods will be discussed later in further detail.

Studies have been made comparing the cost of transporting energy as hydrogen via pipeline rather than as electricity in overhead high voltage lines. An English report (22) concluded that with present technology of electrolysis and energy transmission, electricity was more efficient than hydrogen as an energy carrier. This study assumed electricity has a higher average "usefulness" per unit of energy. With current capital cost estimates, they found that only at transmission

distances greater than 2000 kilometers might hydrogen be a more economical fuel to produce and transport.

The examination of energy transmission in the American Gas Association report was much more optimistic. They based conclusions on development of increased efficiency of hydrogen production and showed that possible future savings in energy justify further examination of hydrogen as an alternative fuel.

Leeth, in a recent study (41), concluded it may be more efficient to use nuclear heat to produce hydrogen rather than electricity. His study considered capital cost of equipment and energy lost in transmission. Because of high loss of energy in electricity transport he concluded that thermochemical hydrogen could be produced and transported more cheaply than electricity over distances greater than 100 kilometers.

Transmission of energy over longer distances will become more important as the emphasis on building larger nuclear reactors continues. Social pressure will mean location of these power generating stations further from population centers.

Hydrogen production offers the possibility of storing energy during periods of low demand. Hydrogen generating equipment can be operated uniformly with excess gas being stored for use later. Design of present electric plants requires a "load use" factor which allows the facility to meet peak periods of demand, which occur only during certain hours of the day and certain seasons. Since electricity cannot be stored, but must be used as it is produced, the power plant equipment with

high capital investment cost cannot be utilized at full capacity except during the peak demand periods.

Storage of hydrogen can be accomplished in much the same way as natural gas is presently stored. Such methods of storage have disadvantages in that hydrogen is a less energetic fuel than natural gas and requires larger volumes to store the same amount of energy. Underground storage of hydrogen at 700 psia will have about one-quarter of the energy capacity of natural gas (21).

Cryogenic storage of hydrogen is possible but is also more costly than for natural gas because of the low boiling point of liquid hydrogen. A third method involves the storage of hydrogen chemically as metal hydrides (61). Some hydrides can store large amounts of hydrogen which can be released simply by gentle warming. The disadvantage of such a system is the large inventory and weight of the metal required.

Optimistic supporters of a hydrogen economy maintain that the fuel can be used in a wide variety of applications. Initial impact of hydrogen could be anticipated in areas where large amounts of natural gas are presently consumed, home heating and cooking. In some areas of Europe, pipeline gas is already approximately 50% or more hydrogen gas. Technological changes in the types of burners used are needed before complete conversion to hydrogen can be initiated. Catalytic devices which burn hydrogen can be used but these require development of inexpensive catalysts which are not easily poisoned.

Hydrogen has also been suggested as a possible fuel for application in automobiles where its use could do much to alleviate pollution in cities such as New York and Los Angeles where automobiles have often

been cited as a major source of air pollution. The exhaust from an internal combustion engine which operates on hydrogen not only has no unburned hydrocarbons but significantly lower levels of nitric oxides. Studies by Schoeppel (55) have shown that an internal combustion engine can be easily modified to operate on hydrogen fuel. The modification would allow the engine to use hydrogen fuel in areas of high population density where pollution is a problem, but switch to conventional fuel in areas where longer range is needed. Difficulty in carrying large amounts of hydrogen in automobiles severely limits the operating range of a vehicle.

For these and other reasons the use of a hydrogen fuel intermediate has been gaining considerable support from concerned scientists around the world. The primary question to which most work has been addressed has to do with the production of hydrogen for use as a fuel. If it is assumed hydrogen will be used as an energy carrier, what is the most efficient method of generating hydrogen from water? The different methods of producing this synthetic fuel will be briefly discussed, noting the major points of each.

Electrolysis

Production of hydrogen from water basically involves carrying out the following reaction:

At 298°K and one atmosphere pressure this reaction has an enthalpy change of + 68.32 kcal/mol (285.85 kJ/mol) of which 56.69 kcal/mol

(237.19 kJ/mol), the free energy change, must be provided as work.

Electrolysis of water uses electricity to provide the free energy change of reaction.

Electrolysis is the only method used on a commercial scale which splits water into its elements. The process is handicapped by the inefficiencies of converting heat to electricity as well as imperfect cell performance. Defining cell efficiency as the ratio of the heating value of hydrogen to the electrical energy input, present cells operate at 60 to 70% efficiency (21). Couple this with the 30 to 40% efficiencies of modern steam generating electric plants and one gets an idea of the energy inefficiencies inherent in electrolytic hydrogen production. Further criticism is raised by consideration of the high capital investment required for a large-scale electrolysis plant. Such an operation requires both electric generating equipment and expensive electrolysis cells.

Worldwide electrolysis accounts for roughly three million pounds of hydrogen per day which is only 3% of the total hydrogen used in the United States (29). Most of this production is in areas where natural gas is quite expensive but electric power is available at low cost. These areas include Chile, Norway, Egypt, and India.

Generation of hydrogen by electrolysis is attractive for storing off-peak power, particularly from nuclear reactors. Such storage could help eliminate the low use factor system needed to satisfy peak demands. Hydrogen generated during low use period could be used in fuel cells, providing electricity during peak periods, thus making full use of existing nuclear facilities.

The most important factor in the overall process efficiency is related to the production of electricity. Before electrolytic hydrogen will be a viable alternative energy carrier improvements in the generation of electricity are needed. However, since there are some who expect conversion of heat to electricity may someday reach an efficiency of 50 to 55% of the ideal, there is hope that an overall hydrogen production efficiency on the order of 50% may be realized.

Thermochemical Cycles

Searching for methods of hydrogen production more efficient than electrolysis has prompted many people to propose thermochemical processes to split the water molecule. The thermal decomposition of water can be accomplished by a single step at extremely high temperatures (greater than 2000°C), or by a series of chemical reactions each at lower temperatures. Since the highest temperature outlet expected from advanced nuclear reactors will probably be 1000 to 1300°C (4) it is hoped that a series of reactions each at some temperature less than 1000°C can be found, whose net result is the decomposition of water to hydrogen and oxygen. To minimize the environmental impact of such a process, the series of reactions must form a closed cycle. This implies all materials will be internally recycled. Water would be the only compound consumed and only hydrogen and oxygen would be produced.

An example of such a proposed thermochemical cycle is the Mark-1 cycle proposed by Gianfranco DeBeni in 1969 (31, 32). It consists of a series of four chemical reactions:

Which sum to give;

Clearly each reaction is within the temperature limits of the heat source, and all intermediate chemical species have been recycled.

Since any thermochemical cycle produces an amount of useful work equal to the standard Gibbs free energy change of formation of liquid water, thermodynamics limits the efficiency any cycle can attain. The minimum amount of heat absorbed at the higher temperature is given by;

$$Q = - \Delta G_f (\text{H}_2\text{O} (l)) \cdot \left(\frac{T_{\max}}{T_{\max} - T_{\min}} \right)$$

This is a consequence of the second law of thermodynamics which limits the amount of useful work obtained from any heat process (14, p. 32).

Defining an efficiency for hydrogen production, η , as the ratio of the total energy required to dissociate liquid water at 298°K

$(\Delta H_{fo} (\text{H}_2\text{O} (l)))$, to the total heat absorbed by the overall process, Q , we obtain the generally accepted (1, 19) figure of merit;

$$\eta = \frac{\Delta H_{fo} \text{H}_2\text{O} (l)}{Q}$$

Which is ideally given by,

$$\eta = \frac{\Delta H_{f^o} \text{H}_2\text{O}(1)}{\Delta G_{f^o} \text{H}_2\text{O}(1)} \cdot \left(\frac{T_{\max} - T_{\min}}{T_{\max}} \right)$$

The ideal figure of merit is greater than the efficiency of a Carnot Cycle (ideal reversible work cycle) because a portion of the energy required to dissociate water can be provided as heat. This follows from the relation;

$$\Delta H = \Delta G + T\Delta S$$

where $T\Delta S$ can be provided as heat.

In selecting reactions for a thermochemical cycle one would prefer a set of reactions all having free energy changes close to zero or slightly negative. This insures a favorable equilibrium yield since;

$$\ln K = \frac{-\Delta G}{RT}$$

where T is the thermodynamic temperature, R is the gas constant and K is the value of the equilibrium constant. Funk has demonstrated (19) that such a cycle is theoretically possible, from a consideration of just the thermodynamics of an ideal set of reactions. Thus it is possible to find a multistep chemical process which requires no useful work input yet has favorable equilibrium yields.

To date there are no thermochemical processes developed which are producing hydrogen from water and most research is in preliminary stages of development. A partial listing of thermochemical cycles can be found in Appendices I, II, and III. In many cases little is known about the feasibility of many of the proposed reactions, either reliable thermodynamic data is unavailable or nothing is known about kinetics or possible side reactions. Attempts to make efficiency estimates in the

absence of such information have resulted in the reporting of inconsistent evaluations of the different processes. In addition to the heat required for the reactions any meaningful figure of merit must account for any separation work as well as process requirements for compressor, pumping and mixing work. Since few thermochemical cycles have been developed to where such a complete evaluation can be made, any estimate of efficiency must be regarded cautiously.

Figures of merit, η , reported in the literature range from 49 to 18% (10, 52). Thus the potential for better efficiency than with electrolysis certainly exists. Increased efficiency has two benefits, the obvious being a greater conversion to useful energy. Estimates have suggested that even a 1% increase in efficiency would result in an annual savings approaching one billion dollars, if hydrogen were to replace natural gas and gasoline (29, p. 33). Not so obvious, however, is the savings in waste heat, since any efficiency is also a measure of how "dilute" the heat rejected to the environment will be. The larger size of proposed power plants means more concentrated thermal pollution from waste heat, a problem which can only be solved by increased efficiency.

A third possible method of generating hydrogen is to combine a thermochemical cycle with an electrolytic step. A problem with many thermochemical cycles is that they involve one or more steps which have unfavorable thermodynamics and require some work to give favorable yields. In some cases improved efficiency might be realized if electrolysis was employed to provide the work needed. Appendix III lists some combined thermochemical electrolytic processes. Obviously

this would only be the case if the work required was substantially lower than the 56.7 kcal/mol required for direct water splitting.

Thermochemical hydrogen producing cycles have valuable potential for providing effective means of converting heat to an ideal intermediate energy carrier. Lack of experimental or theoretical demonstration have limited the usefulness of most evaluations to date. A time study compiled by Chao (10) shown in Figure 3 shows a future advantage for thermochemical hydrogen processes over other closed cycle methods of hydrogen generation. Realization of this advantage depends on the development of an efficient thermochemical cycle.

Reverse Deacon Reaction and Alternatives

The reaction of chlorine and water vapor to yield oxygen and hydrogen chloride at high temperature has formed the basis for a number of thermochemical cycles (Appendix I). This reaction written as;

is the reverse of the Deacon process which has been used industrially to produce chlorine from hydrochloric acid. Thermodynamics show the reverse reaction (above) to be favored at temperatures greater than 860°K and at 1000°K the theoretical equilibrium conversion of chlorine is about 65%. The reaction's endothermic nature makes it well suited for use in thermochemical cycles for the reaction "gains" some for us in the dissociation of water.

Figure 4 illustrates what is meant by a "gain" in thermodynamic terms. As mentioned previously, the dissociation of water into its

Figure 3. Estimated future energy costs (10).

Figure 4. Enthalpy as a function of temperature for $H_2O_{(g)}$, $HCl_{(g)}$, $H_2 + Cl_2$, and $H_2 + \frac{1}{2} O_2$.

elements requires a large amount of free energy. Hydrogen chloride dissociation, however, has a lower free energy requirement as shown in Figure 4. A suggested thermochemical-electrolytic process involves formation of hydrogen chloride by the reverse Deacon reaction followed by electrolytic dissociation to yield hydrogen and chlorine;

The reverse Deacon reaction cannot be implemented without some technological innovation. One problem arises as a result of the corrosive nature of the gaseous mixture, improvements of process materials will be required to handle it at such a high temperature. Also, since conversion will not be complete, the gases will need to be separated. Separation will have to be done in such a way as to prevent a shift of products (O_2 and HCl) back to reactants (Cl_2 and H_2O). This shift is favored at the lower temperatures where separations will probably be done. Furthermore, the techniques of separation will need to have low energy requirements and be highly selective. Oxygen leaving the system must be pure enough to avoid significant loss of chlorine from the system.

The reverse Deacon reaction also needs development of a catalyst which will function at the high temperatures suggested. Copper chloride catalysts have been developed for the Deacon process, but they cannot function at temperatures in excess of 500°K due to increased volatility (57, p. 252). Mixtures of rare earth chlorides and copper chloride have been suggested for use because of better stability at higher temperatures (3, 50). Any process development will need to be concerned

with loss and recovery of the catalyst if the high reactor temperatures are to be realized.

In order to avoid some of the problems associated with processing the reverse Deacon reaction, some people have suggested other reaction systems which perform the same function but do so in two or more steps. An example is the two reaction sequence proposed by Wentorf and Hanneman (64) as part of their Agnes cycle. This sequence uses compounds of magnesium to liberate oxygen and produce hydrogen chloride;

The temperatures indicated are those which they suggest. The first reaction is a simplification of what actually occurs, for it involves absorption of chlorine into an aqueous slurry of magnesium hydroxide to form hypochlorite ions. These ions are then catalytically decomposed to release the oxygen. This thesis contains experimental results indicating such a reaction is indeed possible. Such things as catalyst concentration, possible side reactions and operating temperature have been examined.

Criticism of this system was raised by Abraham and Schreiner (1). Doubting that the above reactions would go as written led them to propose a third alternative to the reverse Deacon system. Their two step system and possible operating temperatures are given by;

In such a system chlorine reacts with magnesium oxide to liberate the oxygen and form anhydrous magnesium chloride. In a second reaction, magnesium chloride can be contacted with steam at high temperature to form hydrogen chloride and magnesium oxide, which can then be recycled. This second reaction has been used commercially to produce a high quality magnesium oxide from magnesium chloride brines. A high degree of conversion is possible at the temperature suggested (800°K) (51, 56). There is little information available regarding the reaction between chlorine and magnesium oxide. Although thermodynamics predicts a favorable yield of oxygen at ambient conditions one wouldn't expect the reaction kinetics to allow the reaction to proceed rapidly at such temperatures.

The reason for proposing any alternative to the reverse Deacon reaction is the goal of increased efficiency. Which of these proposals would be the most efficient? By examining the various alternative systems one can detail the merits and defects of each. From this information a process flowsheet can be constructed which dictates heat and work requirements. These requirements estimate the relative efficiency of each alternative.

EXPERIMENTAL INVESTIGATION

Purpose

The magnesium hydroxide reaction with chlorine has been examined experimentally to determine the conditions which favor the production of oxygen. In proposing this reaction as a possible step in a thermochemical cycle, Wentorf and Hanneman mentioned briefly a method of operation which would release oxygen and form magnesium chloride hydrates. This process involves the formation of hypochlorite ions by reacting chlorine with an aqueous magnesium hydroxide slurry. Presence of a "basic hydrated cobaltic oxide" (64) will catalyze the decomposition of the hypochlorite, liberating oxygen. They also note that some tests indicate absorption of chlorine into the solution to be the rate limiting step. Wentorf and Hanneman imply that by limiting the amount of water present it might be possible to form as a product monohydrates of magnesium chloride. The conditions which might allow for this were not mentioned (64).

In this present investigation the attempt was made to confirm the feasibility of such a proposal. Could oxygen be liberated from magnesium hydroxide using such a scheme? If so would it be free from large amounts of chlorine? Another important question involves separation of magnesium chloride from the product solution. Can the monohydrate be obtained from the product solution without using evaporation and dehydration steps? The heat requirements for evaporation and dehydration would severely penalize the efficiency of such a process.

Contacting chlorine gas with a caustic solution rapidly produces hypochlorite ions by the following reaction;

which may be regarded (48, p. 565) as a two step sequence which proceeds as follows;

Chlorine water, a solution of dissolved chlorine in water contains equimolar amounts of the weak acid HOCl and the strong acid HCl. The equilibrium constant (24, pp. 275-300) for the oxidation reduction reaction, K_{eq} ;

$$K_{\text{eq}} = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]}$$

has been calculated to be $10^{-4.5}$, implying low conversion and a weakly acidic solution. The neutralization reaction, however, proceeds almost completely to the right, as indicated by a favorable equilibrium constant of $10^{+20.3}$ for;

$$K_{\text{eq}} = \frac{[\text{ClO}^-]}{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}$$

The spontaneous nature of the neutralization reaction drives the overall reaction to completion favoring formation of the hypochlorite in a basic solution.

Formation of hypochlorite ions in a basic solution of magnesium hydroxide is hampered by the low solubility of the hydroxide. In a water solution the solubility product constant for magnesium hydroxide

is $10^{-11.1}$ (24, p. 565). From this an equilibrium constant of $10^{+4.8}$ has been calculated for the overall reaction;

Thermodynamics then predicts, provided the reactants and products are at standard concentrations (gases at 1 atmosphere, solution 1M), the equilibrium will favor formation of hypochlorite ions.

Calcium hypochlorite solution, a bleaching solution used in large quantities by the paper industry is produced by chlorination of a slurry of slaked lime, CaO . Absorption of chlorine is quite rapid and chlorination towers can easily provide adequate contact for complete absorption of chlorine (37, p. 146). Since magnesium hydroxide reacts in a similar manner, it is believed that development of a system which absorbs chlorine effectively should pose no major problems.

Decomposition of the hypochlorite is given by the reaction;

The large value of the equilibrium constant is a measure of the instability of the hypochlorite ion in solution.

Liberation of the oxygen trapped by the hypochlorite is favored by the presence of a suitable catalyst. Heavy metals salts are generally excellent catalysts in solution reactions involving oxidation and reduction. Cobalt ions, Co^{++} , and to a lesser extent ferric, nickel, cupric, and manganese ions, will all decompose hypochlorite ions (6, p. 473). Although the processes by which these metals promote reactions are quite complex they are believed to be the results of the ability of the metal ions to exchange electrons readily (66, p. 71).

A laboratory method for preparing oxygen (39) consists of adding a salt of cobalt to a solution of calcium hypochlorite and heating the solution almost to boiling (80°C). The cobalt chloride is immediately converted to cobalt oxide, the cobalt species which catalyzes the hypochlorite decomposition. Cobalt salt is converted to the oxide in an alkaline solution in two steps given by (39);

Spontaneous conversion of hypochlorite into chloride and chlorate, a possible side reaction, is a matter of considerable importance since three moles of oxygen are trapped by each mole of chlorate which forms. This reaction;

has a favorable equilibrium constant at 298°K and standard conditions (65). Disproportion of hypochlorite becomes more significant at higher temperatures. Potassium chlorate, a powerful oxidizing agent, is made commercially by chlorination of a hot concentrated solution of potassium hydroxide (48, p. 566). Heating of any hypochlorite solution will result in a substantial conversion to form chlorate. Decomposition of chlorates to release oxygen will not occur in solution using any known catalysts (49). Magnesium chlorate crystals, however, are unstable above 120°C (63, p. B-191), and will release trapped oxygen. Recovery of the oxygen held by chlorate will necessitate additional process handling and it is therefore desirable to determine the conditions which minimize the formation of the chlorate ions.

Lister (43, 44) has examined the decomposition of sodium hypochlorite in both catalyzed and uncatalyzed reactions. In an uncatalyzed system disproportion to form chlorate occurs with little simultaneous unimolecular decomposition to yield oxygen. His study of the kinetics confirmed the mechanism of Foerster and Dolch (18) for the observed rate of reaction. This mechanism involves formation of an intermediate chlorite ion as the rate limiting step. A bimolecular reaction between chlorite and hypochlorite then occurs to form chlorate. The mechanism is thus given by;

Many articles have dealt with the effect of solution pH on the rate of reaction (45). Chapin has reported (11) disproportion to give chlorate to be most favorable at a pH level of 6.8 with hypochlorite stability increasing in both strongly acidic and basic solutions. Lister concluded the rate of reaction to be independent of pH provided solutions had equal ionic strength (43).

The catalyzed decomposition reaction studied by Lister involved addition of 1.0-4.0 milligrams of a metal salt to a one liter solution approximately 1 molar in hypochlorite ions. These salts included manganese chloride, ferric nitrate, cobalt chloride, nickel chloride and copper chloride. The manganese salt was ineffective in catalyzing the release of oxygen and iron was only slightly effective. Cobalt, nickel and copper all successfully decomposed the hypochlorite solutions under the conditions of the experiment (30-60°C). The effect of catalyst

on the disproportion reaction was examined by comparing the chlorate concentration observed without catalyst to that with catalyst present. Lister concluded that in no case was the chlorate reaction catalyzed. This suggests a mechanism which does not involve the formation of any chlorite intermediate. Catalysis probably occurs through oxidation of the metal to a higher unstable oxide which decompose to release the oxygen. Since neither iron or manganese have unstable higher oxides they are unable to catalyze the reaction. The fault of this theory is that it predicts an unreasonably high rate of decomposition for the higher oxidation state (43).

A simple mechanism proposed to explain the catalysis, is given by;

Little study of the effect of hypochlorite concentration on reaction rates have been conducted. Most research has involved solutions with hypochlorite concentrations greater than one molar with additions of small amounts of catalysts (less than 5 milligrams of catalyst as salt). Under these conditions the reaction rate was found to be independent of hypochlorite concentration, and thus most workers concluded a step such as C above to be rate controlling. Lister in his report concluded that the catalyst surface was probably covered and thus the rate of oxygen evolution depended only on the amount of catalyst present.

Studies involving lower concentrations of hypochlorite and greater amounts of catalysts were not found in the literature. Such studies are not well suited to kinetic investigations because of the difficulty of maintaining a measurable hypochlorite ion concentration in solution.

In a system such as that suggested by Wentorf and Hanneman (64) it would be desirable to decompose the hypochlorite ions as rapidly as they form, and thus a higher concentration of catalyst will be needed. Maintaining a low hypochlorite concentration will minimize the decomposition to form chlorate.

The temperature at which the system might best operate needs to be determined. Catalyst activity to decompose hypochlorite and release oxygen is favored at higher temperatures, however, so is the conversion to form chlorate. What temperature can the system be operated at without considerable formation of chlorate?

Conditions which might favor production of a monohydrate of magnesium chloride seem unattainable. Table 1 lists the form of magnesium chloride crystals which are in equilibrium with a saturated solution under various conditions (42). Only at temperatures greater than 100°C can anything better than a hexahydrate be obtained, and no conditions are listed which mention an equilibrium solution with monohydrate crystals. Since the reaction of magnesium hydroxide with chlorine produces a mole of water the initial mixture must be anhydrous in order to obtain only a monohydrate as a product. The reaction cannot then occur in solution and form a monohydrate.

Experiments were conducted to answer these questions raised. Equipment was constructed which contacted a known flow rate of chlorine

Table 1. Solubility of MgCl_2 in water (42, Vol. II, p. 480)

Temperature °C	Grams MgCl_2 per 100 gms. sat. sol.	Solid phase in equilibrium
0	34.6	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
20	35.3	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
40	36.5	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
60	37.9	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
80	39.8	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
100	42.3	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
116.7	46.2	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
130	48.6	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
150	51.8	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
170	54.6	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
181.5	55.8	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} + \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
200	56.8	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$

with a slurry of magnesium hydroxide and allowed for any gas produced to be collected and measured. Among the parameters examined were i) the amount of catalyst required to decompose the hypochlorite which forms, ii) effect of temperature on chlorate conversion, iii) possibility of operating the experiment in a concentrated magnesium chloride solution and iv) oxygen liberated as a function of chlorine input. Several analytical techniques were employed to obtain quantitative measurements, each of these will be described briefly. Hypochlorite, chlorite and chlorate ion concentrations were all measured under a variety of

conditions. Spot tests for hypochlorite and chlorate were also used on occasion.

Analytical Techniques

Spot tests were used on occasion to detect the presence of hypochlorite or chlorate ions. These tests were as follows;

a. Test for hypochlorite with thallous hydroxide (17, p. 149).

Thallous hydroxide, a colorless water soluble compound reacts with hypohalogenites in a solution to form a brown insoluble thallic hydroxide. The reaction proceeds as below;

The test is affected by the presence of peroxides, however, hypochlorite cannot coexist in a solution with peroxide present.

The procedure involves soaking filter paper in a 2% solution of thallous sulfate and drying. If a drop of test solution is applied to a small piece of the reagent paper, a brown stain will appear if hypochlorite is present. Such a test will detect as little as 0.5 micrograms of hypochlorite.

b. Test for the presence of chlorate with manganous sulfate and phosphoric acid (17, p. 182).

Chlorate ions react with manganous sulfate in a concentrated phosphoric acid medium to form complex manganese III phosphate anions. These anions form in the reaction;

and give a violet coloration to the solution.

The mechanics of the test involve preparing a solution of half manganous sulfate and half syrupy phosphoric acid. A drop of this solution is mixed with a drop of test solution in a small porcelain dish. The mixture is briefly warmed and allowed to cool. Appearance of a violet color indicates presence of chlorate in the sample. The limit of identification is 0.05 micrograms of chlorate.

Quantitative tests were used to measure concentrations of chloride, hypochlorite and chlorate ions. These tests are explained below;

c. Mohr titration to measure chloride ions (15, 59).

Chloride ions react with silver nitrate to form silver chloride, a relatively insoluble white precipitate.

The end point of the titration is indicated by the appearance of a red precipitate of silver chromate. Silver chromate being more soluble than silver chloride will not appear until all the chloride is precipitated. The reaction forming silver chromate;

depends somewhat on the pH of the solution as well as the concentration of the chromate ions in solution. The details will not be included here except to note that the test is most favored at pH of 8.0 and a chromate concentration of 0.005 molar.

The procedure involves preparation of solutions of silver nitrate of known normalities. Samples to be tested for chloride (10 to 20 ml size) are diluted to 100 ml with deionized water. Five milliliters of 0.2 M solution of sodium chromate is then added as the indicator.

A small amount of calcium carbonate is added to maintain the proper solution pH. The titrating solution of silver nitrate is then added dropwise until the first appearance of a slight red-orange color.

The Mohr titration is an excellent method of determining chloride ion concentration, the technique is quite precise and accurate.

d. Quantitative hypochlorite measurement (2, p. 468).

Hypochlorite solutions, strong oxidizing agents, react with arsenious trioxide to give the pentoxide (4).

In a basic solution only the hypochlorite reacts with arsenious oxide in this way (5). A sample (10 cc) to be measured for hypochlorite is added to 15 ml of a 1% sodium hydroxide solution. An excess of a 0.10 N solution of arsenious oxide is added to the solution and allowed to react with the hypochlorite present. Enough sodium bicarbonate is added to keep the solution saturated. The amount of unreacted arsenious oxide can be determined by titrating with a standard iodine solution using a starch-iodide indicator.

The results obtained from this technique were fairly good, however, the iodine solution must be standardized each time it was used because of deterioration which occurs with time. This deterioration actually caused an increase in the strength of the iodine solution.

e. Chlorate measurement using arsenious oxide (38, p. 849, 852).

Chlorate ions will react with an arsenious oxide solution in a concentrated hydrochloric acid medium with a small amount of iodine monochloride present as a catalyst (45). The iodine monochloride is

important to insure rapid reaction with the arsenious oxide. The procedure involves addition of an excess amount of arsenious oxide to a sample (10 cc) to be measured for chlorate concentration. Two ml of 0.008 M iodine monochloride in 6 M hydrochloric acid and 20 ml of concentrated hydrochloric acid is then added to promote the reaction. The mixture is then boiled briefly and allowed to cool. The excess arsenious oxide can be titrated with potassium bromate using a methyl orange indicator.

This procedure was found to give inconsistent results, particularly when trying to measure low concentrations of chlorate (less than 10^{-3} M). These inconsistencies were greatly influenced by the amount of boiling the solution was subjected to before the titration was carried out. When a portion of arsenious oxide was boiled for an extended period in a concentrated hydrochloric acid medium the oxide was completely converted to the pentoxide (As_2O_5) even if no chlorate was present.

f. Hypochlorite and chloride (59).

These ions were measured together by decomposing the hypochlorite with the addition of a small amount of hydrogen peroxide. The hydrogen peroxide reacted to liberate the oxygen by the following reaction;

The total chloride ion concentration was then measured using the Mohr Technique (above). The chloride ions measured were the sum of the hypochlorite ions and chloride ions in the solution. This procedure could not be used with free chlorine present in the system because of

a reaction which occurred between the halogen, the chromate indicator and the hydrogen peroxide.

Equipment and Procedures

Figure 5 illustrates the equipment setup used to study the magnesium hydroxide reaction with chlorine. The system was designed to contact a stream of chlorine gas with a slurry of the hydroxide. The potassium iodide solutions shown trapped any excess chlorine leaving the reaction flask. Any gas produced by reaction exited the system and was collected in an inverted graduate cylinder.

The chlorine gas cylinder was purchased from the Matheson Gas Company and fitted with the proper regulator. Different types of tubing were tested and the effect of chlorine on each noted. Tygon R-3603 reacted slowly with the chlorine gas used. This could suggest the presence of trace amounts of water in the chlorine gas since the Tygon tubing was allegedly safe for use with "dry" chlorine. Glass and teflon tubing appeared to be inert to chlorine.

The rotameter used was a Lab-Crest Model 448-035 which had a flow range of approximately 5 to 40 cc/min of air. A calibration for chlorine was obtained by reacting a stream of chlorine at a constant rotameter reading with a solution of sodium hydroxide. The chlorine reacted to produce chloride and hypochlorite ions. By measuring the concentrations of these ions the total flow of chlorine at that particular rotameter setting was calculated. Such a procedure was time consuming but gave a calibration curve with good reproducibility.

Figure 5. Experimental apparatus.

A serious problem with the system was the tendency of the rotameter to "foul" with the float becoming stuck to the walls of the rotameter. This generally would occur only after chlorine had been passed through the rotameter for 1 to 2 hours. It was believed to be caused by trace impurities in the chlorine stream which condensed on the walls of the rotameter. Nothing was found to alleviate the problem and the source of the impurities could not be determined. Only in the experiments of longer duration did this cause difficulties, causing some experiments to be terminated earlier than anticipated.

The chlorine stream contacted the slurry via the simple sparger tube arrangement shown in Figure 5. This feature severely hindered effective gas-liquid contact and limited the flow of chlorine to low levels (10 to 40 cc/min).

The reaction flask was submerged in a water bath with temperature maintained by a Sargent Welch thermonitor. Temperature regulation was generally $\pm 0.25^{\circ}\text{C}$.

The half liter reaction flask was charged with a maximum of about 400 ml of solution. Agitation was provided by a magnetic stirring bar driven by an external source. Pressure was monitored by connection to a water manometer and temperature measured using a mercury bulb thermometer.

Gas which exited the flask passed through a water cooled reflux condensor preventing significant loss of water. This gas was then bubbled through a series of two 500 ml solutions of potassium iodide to remove any chlorine in the exit gas. Potassium iodide reacts rapidly chlorine in solution to form soluble potassium chloride and free iodine,

I₃⁻. Release of the iodine was detected by the appearance of a dark amber color. This method was very effective for removing all the chlorine in the exit gas stream. In only a few cases was any chlorine detected in the second potassium iodide trap. Finally the gas which passed these solutions exited the system and was collected in an inverted graduate cylinder where its volume was determined.

The procedure for each experiment differed depending on the parameters to be examined. In general a solution to be chlorinated was charged with a measured amount of magnesium hydroxide (Fischer Scientific Laboratory Grade). Cobalt chloride was added to the mixture as a solution prepared from cobalt chloride hexahydrate crystals (J. T. Baker Chemical Company, Baker's Analyzed). Following this an appropriate amount of deionized water was added to give a total addition of 400 ml of water. The reaction vessel was then placed in the temperature bath and the solution temperature allowed to come to equilibrium, this usually required about 15 to 20 minutes. The appropriate connections were then made and tested for leaks using argon gas to pressurize the system. The system pressure was determined by the liquid head in the potassium iodide trapping solutions. Provided no leaks were found chlorine flow was initiated and the test begun. Monitoring the gas flows as a function of time involved recording rotameter readings and the level of the water in the collecting cylinder.

When the experiment was finished samples of liquid were removed and centrifuged to remove suspended magnesium hydroxide and the insoluble cobalt catalyst. Ion concentrations were then measured using the appropriate analytical technique.

Results and Discussion

Catalyst

Cobalt chloride was the catalyst used in these experiments to study the decomposition of hypochlorite. Solutions of cobalt chloride were tested separately with each compound in the system to detect any reaction which might occur. A cobalt chloride solution was contacted with a stream of chlorine gas and, as expected, no interaction occurred.

Addition of cobalt chloride to a strong alkaline solution (NaOH) gave rise to the formation of a precipitate of cobalt hydroxide ($\text{Co}(\text{OH})_2$). However, no such reaction was observed in a solution of magnesium hydroxide which was only slightly basic. No reaction was noted between cobalt chloride and the products oxygen and magnesium chloride.

Contacting the cobalt salt with hypochlorite ions caused an immediate brown-black precipitate to form. This precipitate was the cobalt oxide species which catalyzes the reaction. References in the literature disagree on the exact nature of the oxide which such a reaction forms. $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{CoO} \cdot \text{OH}$ were reportedly isolated by Hüttig and Kassler (28). Other possible species include Co_3O_4 , CoO , and Co_2O_3 (39). An experiment was performed to obtain a sample of the oxide large enough to test by X-ray diffraction techniques. The experiment involved completely reacting a small amount of magnesium hydroxide (approximately 2.5 grams) with chlorine in a 400 ml solution with excess cobalt chloride present (about 5 grams). After all the hydroxide had reacted, the precipitate remaining was washed to remove traces of

MgCl_2 or CoCl_2 which might be present. The cobalt compound was then separated from solution and dried at 110°C for 24 hours before being ground and passed through a 180 Tyler mesh screen. A qualitative analysis by flame spectrograph showed only trace amounts of magnesium to be present.

X-ray diffraction is an excellent method of identifying species of compounds present in a sample. Since each compound has a unique crystal structure, each will diffract X-rays in a different pattern. The procedure followed is to generate a diffraction pattern from a small sample of powder and then simply identify the intensity bands which appear at different angles of incidence. These bands or peaks depend only on the type of X-rays used and the crystal structure of the sample. Tables are available (16, 62) which list the peaks which correspond to the different compounds, and thus enable one to determine the compounds present.

The samples of cobalt catalyst tested using X-ray diffraction gave a diffraction pattern typical of an amorphous sample, or in other words, one with no crystalline structure. This was not too surprising considering the manner in which it forms. The reactant species, cobalt chloride and hypochlorite are both soluble in water and their mobility enables them to react readily. However, the cobalt oxide product is insoluble, and the molecules of the black precipitate which form are not free to align themselves in a crystalline pattern.

Since the molecules do not bond together and form any definite crystal structure, the catalyst surface area is most probably quite high. A high surface area is an important criterion for the catalysis

of a heterogeneous reaction by an insoluble catalyst. Howell (27) reported a decrease in the catalyst activity in those solutions in which the cobalt oxide was allowed to settle out of the solution and set for a few days. Lister (43) also noted an effect of "aging" which he suspected to be caused by particle agglomeration.

An experiment was performed to test the effect of recycling a portion of the catalyst prepared for the X-ray diffraction test. The sample had been dried, ground and passed through a 180 mesh Tyler screen and might be expected to have a smaller surface area from handling.

In the test an amount of dried catalyst equivalent to an addition of 0.40 grams of cobalt chloride was added to a 400 milliliter solution with magnesium hydroxide present. The molar ratio of oxygen liberated to chlorine flow into the system was significantly lower than for experiments where fresh catalyst had been added. Table 2 lists the average ratio of flows for several cases. These average values were all determined between 40 and 80 minutes into the experiment, this is important to note because, as will be shown later, steady state is not always attained.

An experiment to test the effect observed by Howell and Lister showed no decrease in catalyst efficiency after allowing the black precipitate to settle out and stand for a few days. The oxygen flow rate (Table 2) although slightly lower was within experimental variation of those experiments in which fresh cobalt oxide had been generated. The amount of catalyst (1. to 5. mgm. in one liter of solution) used by Lister and Howell was so much lower than that used

Table 2. Effect of recycling catalyst

Treatment	Experiment	Average ratio of flow moles O_2 ($\frac{\text{moles } O_2}{\text{moles } Cl_2}$)
Freshly prepared catalyst	XIV A	0.357
Freshly prepared catalyst	XXI	0.466
Freshly prepared catalyst	XXII	0.429
Catalyst allowed to settle for 2 days	XV A	0.393
Catalyst dried and ground to 180 mesh	XII	0.240

in these tests that the slight effects of any lower catalyst activity could most probably not be detected.

These tests suggest possible process problems which may arise if the catalyst must be separated from the product. If filtration techniques are used to separate the cobalt catalyst a decrease in efficiency may result from particle agglomeration, particularly if the catalyst is dried. Such a decrease in efficiency implies using a higher inventory. However, any catalyst activity is very closely linked to such things as methods of preparation, techniques of handling, and agitation in solution and it is difficult to predict the overall quantitative effect of recycling the catalyst on a large scale.

Oxygen liberation

In experiments with no cobalt catalyst present the rate of oxygen release was too low to be detected. Chlorine reacts with magnesium

hydroxide to form a hypochlorite solution with no significant oxygen release. Quantitative measurements showed the expected one to one ratio of hypochlorite to chloride concentration. With catalyst present oxygen was released from the hypochlorite as expected. Experiments indicate that at low catalyst levels the rate of oxygen liberation depended on the amount of catalyst present as well as on the hypochlorite concentration in solution. Experiments were performed to investigate the amount of catalyst required to continuously decompose the hypochlorite formed. Comparison between the molar flow ratio of chlorine fed to oxygen released generally showed a less than complete conversion. This was believed to be the result of incomplete chlorine absorption, caused by equipment problems.

A series of several experiments was performed at 50°C to determine what amount of catalyst was necessary to decompose completely the hypochlorite which formed. In each case 400 ml of a mixture containing different amounts of cobalt chloride and 0.10 mole of magnesium hydroxide (5.82 grams) was prepared. After the solution was at thermal equilibrium in the temperature bath, chlorine gas flow between 15 to 20 cc/min was initiated. Records were kept of the rate of chlorine flow into the system as well as the gas being collected at the exit. Generally the magnesium hydroxide was completely reacted after about 120 to 150 minutes of chlorine flow. After 180 minutes, no gas was seen exiting the system and all the chlorine which entered was trapped by the potassium iodide solutions.

Some correction factors had to be applied to the volume of gas collected. The most significant of these was an account for the chlorine

saturation of the "dead space" above the solution and in the lines between the reaction flask and the potassium iodide solutions. The value of this correction was measured by flowing chlorine into the reaction flask with 400 ml of water present. No gas is produced and chlorine fills this dead space pushing the air through the system up to the first potassium iodide solution. The average of two tests showed this correction to be approximately 178 cc of collected gas. Corrections were also made for the oxygen held by the cobalt catalyst. Assuming Co_2O_3 to be the species formed, a significant correction was needed for the larger amount of catalyst used. Table 3 lists the estimated value of this effect for different amounts of catalyst. Gas collected above a water solution was assumed to be saturated with water vapor and a correction for this was applied. This effect lowered the value of oxygen collected by approximately 2%.

Table 3. Correction for oxygen held by cobalt oxide catalyst (assuming Co_2O_3 forms)

Catalyst amount (gms. CoCl_2)	Oxygen held by formation of Co_2O_3 (cc O_2 @ STP)
0.40 gms.	111 cc
0.08	22
0.04	11

Table 4 is a tabulation of the results obtained in this series of experiments. Complete reaction of 0.10 mole of $\text{Mg}(\text{OH})_2$ should have generated 0.50 mole of O_2 (1206 cc @ STP). With additions of catalyst

Table 4. Gas collected at different levels of catalyst (CoCl_2) concentration; temperature, 50°C ; 0.10 mole $\text{Mg}(\text{OH})_2$ reacted to completion (0.05 mole $\text{O}_2 = 1206 \text{ cc @ STP}$)

Experiment #	Catalyst added	Gas collected	Corrected total oxygen ^a	% of expected O_2
XIV h	0.40 gm.	1341 cc	1247 cc	103%
XIV g	0.08	1282	1100	91
XIV f	0.04	1111	911	76
XV f	0.04	1047	869	71
XIV i	0.04	975	779	65
XIV j	0.008	423	234	18
XVII	0.004	287	99	8
XVIII	0.0	206	24	2

^aCorrected for "dead space," water vapor present, and oxygen held by catalyst.

less than 0.08 grams cobalt chloride a dramatic decrease in the amount of oxygen liberated was observed. Three experiments with the addition of 0.04 grams of the chloride salt show that the experimental variation between similar runs was about 5 to 10%. Figure 6 is a plot of the percent of total oxygen released as a function of catalyst concentration.

In these experiments with different amounts of catalyst, gas which exited the system showed a dependence on time. Figure 7 graphs the molar ratio of gas flows (moles O_2 /moles Cl_2) as a function of time for the different amounts of catalyst used. With 0.40 grams of cobalt chloride added, the molar ratio of gas flows was uniform and showed only a large deviation from the ideal ratio of 0.50 at the end points

Figure 6. Percent total oxygen released as a function of catalyst concentration.

Figure 7. Molar ratio of gas flows as a function of time.

of the experiments. Note also that with 0.40 grams of catalyst present the oxygen collected agreed within experimental error with a complete recovery of oxygen from the magnesium hydroxide. These results suggested a catalyst concentration of 1 gram cobalt chloride per liter was adequate to decompose the hypochlorite which forms. In these experiments hypochlorite formed at a rate of approximately 2.10×10^{-3} moles $\text{OCl}^-/\text{min. liter.}$

The results with 0.08 grams of cobalt chloride indicate that early in the experiment oxygen was released more slowly than the chlorine flow dictated. This must have meant an excess of hypochlorite ions built up in solution. As the experiment continued the rate of oxygen release increased, thus apparently the catalytic decomposition was not independent of hypochlorite concentration under these conditions. Using lower amounts of cobalt chloride showed an even more dramatic dependence on time as shown in Figure 7 for the experiments with 0.04 grams of cobalt chloride added. The peak which appears was not caused completely by the effect of increasing hypochlorite concentration. As mentioned, the magnesium hydroxide added (0.10 moles) was completely reacted at about 120 to 150 minutes. After this time excess chlorine began to accumulate in the system and the solution became acidic. Although not completely understood, this phenomena appears to cause a rapid release of oxygen from the hypochlorite accumulated. The peak was not caused by chlorine saturation of the dead space or it would have appeared in all three curves shown. Catalytic activity appears to be favored by either one or all of the following: i) acidic medium, ii) absence of magnesium hydroxide or iii) presence of dissolved chlorine.

In experiments with excess magnesium hydroxide and sufficient catalyst present (0.40 grams cobalt chloride in 400 ml solution) a close to ideal release of oxygen for the input of chlorine was realized. Figure 8 is a plot of the molar flow ratio as a function of time. The scatter shown was caused primarily by difficulty in maintaining a steady flow rate at such a low range of chlorine flow (15 to 20 cc/min). The average of the points shown is approximately 0.450 or slightly less than the ideal 0.500. This value was consistently less than ideal because of incomplete chlorine absorption into the slurry. The sparger tube arrangement used provided poor gas-liquid contact and gas which exited the system always had trace amounts of chlorine present which were trapped by the potassium iodide solution.

Material balance

The results plotted in Figure 8 show little significant difference between the two experiments. Experiment XXI was performed at 50°C while a higher temperature, 80°C, was used in run XXII. A detailed material balance for these two experiments is listed in Table 5, with the total number of moles of each component listed. In both experiments (and all others at the higher catalyst level) no hypochlorite was detected in the solution. Spot tests performed quickly after discontinuing the chlorine flow were all negative for hypochlorite ions.

The chlorine input listed in Table 5 was determined by continuously monitoring the rotameter during experiments. A calibration curve was

Figure 8. Molar ratio of gas flows as a function of time.

Table 5. Material balance (400 ml solution)

Experiment	XXI	XXII
Temperature	50°C	80°C
Chlorine gas input	0.1489 moles	0.09879 moles
Total chloride ions	0.2887 moles	0.17369 moles
Excess chlorine	3%	12%
Hypochlorite ions	None detected	None detected
Chlorate ions	0.0023 moles	0.00042 moles
Total oxygen generated	0.07558 moles	0.00042 moles
{ Oxygen collected	0.06801	0.04154
{ Oxygen held by catalyst	0.0041	0.0041
{ Oxygen held by chlorate	0.00347	0.0006
Error between chloride measured and total oxygen	4.5% high	6.1% high
(Error if no chlorate is generated)	0.9%	4.85%

used to calculate the total input and as expected this input was greater than the chloride ions measured in solution (by Mohr titration).

Measurements of chlorate ions listed are subject to considerable uncertainty. The spot tests were only slightly positive indicating a very low amount of chlorate present. The techniques used to measure chlorate concentration (analytical techniques section) showed only about 3.47×10^{-4} gram equivalent weights of chlorate present in the 10 ml samples tested. A comparison of these estimates with measurements of prepared known amounts of chlorate showed that such a low

amount could simply be "experimental background" error. In those experiments with adequate amounts of catalyst present (0.40 grams cobalt chloride/400 ml) no significant conversion to chlorate was found. Conversion was always less than 1% of the total chloride ions measured, even at experiments at higher temperatures (80°C). Apparently, if hypochlorite ions can be decomposed rapidly to yield oxygen, only trace amounts of chlorate will form. Total oxygen generated was the sum of the three values listed (Table 5). The amount of collected oxygen listed is the corrected value after water vapor was accounted for. The oxygen held by the catalyst and the chlorate was also included as shown. The error between oxygen collected and chloride ions measured was then determined. If the reaction,

went to completion a four to one ratio of chloride ions to total moles oxygen generated should be observed. The errors calculated show the amount of oxygen generated to be in close agreement with the expected value.

Evidence has shown chlorine absorption into the system to be rate controlling under conditions with sufficient catalyst present. This observation concurs with the findings of Wentorf and Hanneman (64). The basis for this was indicated by the failure of any gas to exit the system immediately after the chlorine flow was discontinued. If some other step were rate controlling one would expect to see oxygen being released after stopping the input of chlorine. Moreover, no hypochlorite was detected by the spot tests after the experiment was ended.

These observations, however, do not apply to those systems with insufficient amounts of catalyst present (less than 0.08 grams cobalt chloride/400 ml). In those experiments small amounts of gas left the reaction flask even after chlorine flow was stopped. This was further evidence that a hypochlorite concentration built up with the low amounts of catalyst present.

A final experiment was conducted to determine the feasibility of running the reaction in a concentrated magnesium chloride solution. If such a reaction were possible hexahydrate crystals of magnesium chloride could be obtained directly from the solution without evaporating large amounts of water. This experiment was performed at 80°C. Operating at this elevated temperature would enable one to crystallize magnesium chloride out of solution simply by cooling to lower temperature.

The procedure followed in this test was to prepare a saturated solution from magnesium chloride crystals (J. T. Baker Chemical Company, Reagent Grade). This solution was saturated at 72°C, and therefore contained approximately 39.0 grams magnesium chloride per 100 grams of saturated solution (4.00 M solution). To the reaction flask was added 400 ml of this solution along with 0.733 grams $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.40 grams CoCl_2) and 10 grams of magnesium hydroxide. The addition of the cobalt chloride to the concentrated magnesium chloride solution gave the solution a clear blue-green color, rather than the pink color observed in dilute solutions. The reaction flask was then attached to the system and after the solution temperature stabilized at 80°C chlorine flow was initiated.

Characteristic of most previous experiments was the rapid conversion of cobalt ions to the black insoluble cobalt oxide. This reaction usually occurred as rapidly as hypochlorite was produced. In this test with a concentrated magnesium chloride solution only a very slight trace of cobalt oxide was detected, even after contacting the solution with chlorine for 60 minutes. This slight trace was indicated by a faint dark tint in the otherwise cloudy blue-green mixture. No gas exited the system, while chlorine was continuously absorbed by the potassium iodide trapping solutions. It appeared as though no chlorine was reacting in the flask.

A test showed that addition of hypochlorite to the reaction solution of cobalt chloride in concentrated magnesium chloride resulted in the ready formation of the black precipitate of cobalt oxide. This implies that no hypochlorite was generated by contacting chlorine with a magnesium hydroxide slurry in a concentrated magnesium chloride solution.

Generally absorbed chlorine in solution should, as explained earlier, react to form a weak hypochlorous acid solution which reacts with the hydroxide to produce hypochlorite ions. Since no hypochlorite ions were produced in the solution, this reaction apparently did not occur in the concentrated magnesium chloride solution. It is not completely understood what caused the reaction to be prohibited although several factors are suspected to be responsible.

First the formation of the intermediate hypochlorous acid species was repressed by the high chloride ion concentration present (8.00 M in chloride ions). This can occur from either of two effects. Generally

the solubility of chlorine decreases with increasing chloride ion concentration (9). Although no information was found in the literature regarding solubility of chlorine in magnesium chloride solutions, tests with potassium iodide indicated almost no absorbed chlorine in samples from the experiment with a concentrated MgCl_2 mixture. The second effect is hinderance of the reaction;

by this high chloride concentration, because the equilibrium becomes more unfavorable.

Since the solution was concentrated in magnesium chloride we might have also expected a "common ion" effect to lower the hydroxide concentration in solution. In a magnesium hydroxide solution the OH^- concentration should have been about 2.1×10^{-4} M, but in the concentrated magnesium chloride solution (4.00 M MgCl_2) the hydroxide ion concentration would have only been 1.4×10^{-6} . This decreased concentration, however, is not expected to seriously limit the reaction. The magnesium hydroxide particles were quite finely divided, and a test indicated that they react readily with weak acid even in concentrated magnesium chloride solution.

These tests have shown that chlorine would not react with magnesium hydroxide in a concentrated magnesium chloride solution. The reaction appears to be hindered by the absorption of chlorine and subsequent formation of the hypochlorite intermediate. No investigation was made regarding the maximum concentration of MgCl_2 at which the reaction would occur. Such a study would need to be more concerned with the

method of contacting chlorine with the slurry, requiring development of a different reaction apparatus.

Experimental Conclusions

- 1) A stoichiometric yield of oxygen for the reaction

was realized provided catalyst was present to promote the reaction.

- 2) A sufficient amount of catalyst was found to be about 1.0 gram CoCl_2 /liter. This concentration was adequate for hypochlorite being produced at the rate of 2.10×10^{-3} moles OCl^- /(min. liter).

- 3) The side reaction to give chlorate did not occur to a large extent provided the hypochlorite ions were decomposed rapidly to release oxygen.

- 4) Absorption of chlorine was found to be rate controlling provided adequate catalyst was present.

- 5) The reaction did not proceed in a concentrated magnesium chloride solution. Therefore processing to remove the chloride from solution must include evaporation.

THERMODYNAMICS AND PROCESS CALCULATIONS

The efficiency of a chemical reaction or a thermochemical cycle depends on the total amount of energy required to perform the reaction(s). If the same reaction can be done in two different ways but one requires less energy to perform we define that process to be more efficient. This concept, though certainly nothing unusual in the chemical industry, becomes more important when discussing thermochemical hydrogen producing cycles, for the goal is to manufacture an energy intermediate and to do so in the most efficient manner.

It is with the idea of increasing efficiency that the reverse Deacon reaction, and the various alternatives are to be discussed. In order to compare the different proposals a processing scheme for each has been developed from consideration of the reaction conditions, thermodynamic heat requirements and the equilibrium conversion. These reaction schemes are of a general nature and serve only as a basis for initial scouting of the different proposals. They point out deficiencies of the alternatives as well as suggesting possible methods of avoiding these pitfalls.

To determine the heat and work requirements, estimates must be made of the processing parameters. The thermodynamic constants: enthalpy, entropy and Gibbs free energy have been determined from data available in the literature, particularly Barin and Knacke (5), JANAF (34) and Kelley (36). The relations used to calculate these constants are given by;

$$\text{Enthalpy: } \Delta H = \sum H_f(\text{products}) - \sum H_f(\text{reactants})$$

Entropy: $\Delta S = \sum S_f(\text{products}) - \sum S_f(\text{reactants})$

Free energy: $\Delta G = \Delta H - T\Delta S$

The enthalpy change, ΔH , is a measure of the amount of heat required or liberated by the reaction. If a reaction has a + 10 kJ/mole heat requirement, a process must supply this heat in order to maintain isothermal conditions. The free energy change determines the position of the equilibrium of the reaction (if all species are at standard state) for it is used to calculate the value of the equilibrium constant;

$$\ln K = - \frac{\Delta G}{RT}$$

The equilibrium constant, K , was then used to determine the extent of reaction. Hougen, et al. (26, pp. 1015-1037) have detailed methods for determining the theoretical equilibrium composition of a reaction mixture from the value of the constant K . The approach described accounts for deviation of gases from ideality through use of fugacity correction factors. The general equation;

$$K = \frac{a_B^b a_C^c \dots}{a_D^d a_E^e \dots}$$

where a_i is the activity of the i th component, is an equilibrium expression for the following equation,

Since activity, (a_i) , is related to mole fraction (X_i) , fugacity coefficient (ϕ_i) and total pressure (P) the equilibrium expression can be written;

$$K = \left(\frac{X_B^b X_C^c \dots}{X_D^d X_E^e \dots} \right) \cdot \left(\frac{\phi_B^b \phi_C^c \dots}{\phi_D^d \phi_E^e \dots} \right) P^{b+c+\dots-d-e-\dots}$$

This equation can be applied to any mixture which behaves as an ideal solution. If the reaction is heterogeneous and involves pure liquid or solid components the activity of that component can be taken as unity provided the system pressure is not much greater than the chosen standard state (generally one atmosphere). This simplification becomes more significant when solid or liquid solutions form, for the equilibrium is then greatly affected by the composition of the solid or liquid phase.

The use of an equilibrium constant to predict the final composition also ignores the effect of kinetics or competing side reactions. The equilibrium composition predicted assumes no other components are formed by reaction.

Reactions which give incomplete conversion will require some separation processing to recover the desired product and recycle unreacted components. Separation processes are in general inherently irreversible. Inefficiency results from concentration, temperature, pressure and turbulence gradients which exist in the mechanics of the methods of separation used. In general, however, the amount of work, (W_{sep}), which will be needed to reversibly separate an ideal gas mixture of n components can be calculated from the formula (19, 26);

$$W_{sep} = - RT \sum_{i=1}^n N_i \ln X_i$$

where N_i is the number of moles of component i , and X_i is the mole fraction of that component in the mixture. This equation is a consequence of the entropy change accompanying the isothermal mixing of ideal

gases. In the absence of more rigorous analysis of separation requirements this ideal approach provides a good estimate of the energy necessary.

As mentioned, any actual process will not operate at a high level of efficiency. Benedict (7) in a study of separation processes has estimated the thermodynamic efficiency of ideal distillation as a function of the feed composition. These values are listed in Table 6 and have been derived assuming complete separation of an ideal binary mixture with minimum heat input. Thermodynamic efficiency of ordinary distillation is equal to the ratio of the entropy change in reversible isothermal separation to the minimum increase needed for ordinary ideal distillation. Ideal distillation operates with minimum heat input and minimum reflux ratio.

Table 6. Ideal efficiency of ordinary distillation of a binary mixture as a function of feed composition

Feed composition ^a	Thermodynamic efficiency
0 or 100	0.000
1 or 99	0.056
5 or 95	0.189
10 or 90	0.325
20 or 80	0.500
30 or 70	0.611
50	0.693

^aFeed composition - mole fraction of one component.

Without detailed study of possible separation methods it is difficult, however, to determine what levels of separation efficiency might be realized. The approach adopted by Funk (19) is to estimate an efficiency factor. If it is assumed that such work parallels the efficiency of converting heat to electricity, a factor of between 0.10 and 0.30 might be appropriate. This is roughly 50% of the thermodynamic efficiency listed above for ideal distillation with a feed from 10 to 50% of one component.

These methods of estimating process parameters will be employed to compare the reverse Deacon reaction with the magnesium compound alternatives presented previously. Additional proposals will also be examined briefly.

Reverse Deacon Reaction

The reverse Deacon reaction is a high temperature reaction in which all components are in the gas phase. The major process development difficulties as mentioned previously include discovery of a suitable catalyst and a method of separating the products of the reaction.

The thermodynamics of the reaction have been examined as a function of temperature and the equilibrium calculated from the value of the free energy change. Figure 9 shows the conversion as a function of temperature for the reverse Deacon reaction. At 900°K and one atmosphere pressure the theoretical equilibrium conversion predicts approximately 50% of the chlorine will be reacted for a stoichiometric feed of reactants. Since conversion is not complete, oxygen and hydrogen

Figure 9. Reverse Deacon reaction; conversion as a function of temperature. (Stoichiometric feed of reactants, total pressure 1 atmosphere.)

chloride must be separated from the mixture and the unreacted chlorine and water recycled.

The minimum separation work required has been estimated using the procedure explained above. Table 7 lists the ideal work of separation as a function of conversion assuming one mole each of chlorine and water is fed to the reactor. The total work of separation accounts for the total recycle necessary to produce exactly two moles of hydrogen chloride and one-half mole of oxygen. As expected the total amount of separation work required increases dramatically with decreasing conversion.

The work of separation calculated has been an estimate of the minimum reversible work required. For process comparisons these ideal figures must be corrected to account for inefficiencies. Since the specific separation process to be employed is not known, a range of factors will be applied to estimate the total heat requirements. The lowest efficiency expected might be approximately 10% and the highest perhaps 30%. Assuming equilibrium at 900°K the total energy requirement for separation could vary between 47. kJ/mole Cl_2 reacted and 142. kJ/mole (equivalent to 11.3 kcal/mole and 34.1 kcal/mole respectively).

It has been assumed that heat exchange will be used to heat the reactants up to the temperature of the reactor. If heat can be exchanged at a 95% level of efficiency, approximately 8.70 kJ/mole Cl_2 reacted (2.08 kcal/mole) will be required to maintain a 900°K temperature in the feed to the reactor.

Figure 10 illustrates the process requirements for the reverse Deacon reaction. The heat input or enthalpy change, ΔH , at 900°K is

Table 7. Data calculated for the reverse Deacon reaction

Temperature (°K)	Conversion (% Cl ₂ reacted)	Ideal work of separation ^a at 300°K (kJ)	Recycle ratio	Total work of separation ^b (kJ)
370	1	3.774	100.	377.5
426	2.5	4.144	40.	165.7
473	5	4.611	20.00	92.2
541	10	5.320	10.00	53.2
636	20	6.265	5.00	31.3
722	30	6.830	3.33	22.77
805	40	7.103	2.5	17.76
894	50	7.145	2.0	14.29
1005	60	6.34	1.67	10.56

^aWork to separate the mixture obtained if feed to reactor is a stoichiometric mixture of 1 mole Cl₂ and 1 mole H₂O.

^bTotal work of separation = ideal work of separation × recycle ratio.

Figure 10. Process flowsheet for reverse Deacon reaction.

calculated to be + 59.50 kJ/mole Cl_2 reacted (14.233 kcal/mole). The total energy requirement for the process, including the separation requirements, is thus estimated to be between 115. kJ/mole Cl_2 and 210. kJ/mole Cl_2 .

Actual separation of the products will parallel methods used by the Deacon reaction to produce chlorine. The separation process used will vary depending on how the remaining steps in the thermochemical cycle will use the hydrogen chloride. Some processes use this product in a solution while others require anhydrous hydrogen chloride. In general the gas stream exiting the reactor can be cooled to condense water and hydrogen chloride leaving a mixture of oxygen and chlorine. Separation to obtain pure oxygen can be accomplished by liquefaction of chlorine, however, low temperature (less than the boiling point of chlorine, 238.4°K) will be needed to obtain oxygen of a high purity (35). Liquefaction processes are in general inefficient due to the high amount of compression work required (33).

A second method of separating oxygen and chlorine involves selective absorption of chlorine by sulfur monochloride or carbon tetrachloride (57). Chlorine has a high solubility in sulfur monochloride. At low temperature (- 15°C), almost one mole of chlorine can be absorbed by one mole of the sulfur chloride. The absorbent, rich in chlorine, can then be fractionated under pressure to recover sulfur chloride and liquid chlorine. These methods of separation have all been used commercially to separate the gaseous products of the Deacon reaction,

however, they have never been operated under the conditions of the reverse reaction where an oxygen stream of high purity is the main product.

Magnesium Hydroxide Systems

The reactions involving magnesium compounds have been studied to determine the heat and work which the process will require. The estimates show the process to be handicapped by the high heat requirements for the dehydration and evaporation needed to obtain the dihydrate of magnesium chloride.

Studies show the first reaction;

will occur readily in dilute solution with a catalyst present. The reaction is exothermic in a weak solution (ideal one molar) and liberates approximately + 158.9 kJ/mole Cl_2 reacted (38.0 kcal/mole). In the evaluation published by Wentorf and Hanneman (64) they state the amount of heat liberated can be minimized if the magnesium chloride is obtained from solution as a monohydrate. Experiments showed no reaction in the more concentrated medium and the only conditions which might favor formation of lower hydrates occur at higher temperature and pressure. For comparison purposes two cases will be considered. The first will be that which is thought to be the more realistic, conservative case in which the product of the above reaction is a solution moderately concentrated in magnesium chloride (one to three molar). In a second more optimistic case it will be hypothesized that

under some conditions (higher temperature and pressure) a dihydrate of magnesium chloride might be obtained.

Case I

A magnesium hydroxide reaction system which could be used to replace the reverse Deacon reaction is summarized by the following steps;

The catalyzed reaction to liberate oxygen from magnesium hydroxide occurs readily in solution releasing 158.9 kJ/mole Cl_2 reacted. The resulting solution of magnesium chloride will require evaporation to obtain the hexahydrate crystals from the solution. The heat requirement needed for this evaporation will vary greatly depending on the concentration of the solution (63, p. D-159). Table 8 lists the heat required to obtain one mole of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ from solutions of various concentrations. Assuming a two molar solution, over 20 moles of water must be evaporated for each mole of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ crystals removed. This requires input of 897.4 kJ/mole which alone is more than three times the theoretical amount of energy required to split water into its elements.

Table 8. Heat required to obtain magnesium chloride crystals from solutions of various concentrations

Concentration MgCl_2	Moles water evaporated ^a	Heat requirement (kJ) ^b
0.50	103.8	4572.3
1.00	48.39	2129.9
1.50	29.7	1307.2
2.00	20.38	897.0
3.00	11.03	485.5
4.00	6.33	278.6

^a Moles water evaporated; amount of water evaporated to obtain one mole of magnesium chloride crystals.

^b Heat requirement = moles of water evaporated $\times$ 45.016 kJ/mole.

This evaporation, however, could be carried out using multistage evaporation where heat is internally conserved. The steam of one stage is used to heat the previous stage. Ideally such a system would attempt to perform the following overall reaction;

However, no process could ever succeed in reaching such a low heat requirement, without an infinite number of stages. Commercially up to ten stages have been used, and under these conditions approximately a tenth of the heat requirement for evaporation might be needed. Thus a total input of 89.7 kJ/mole would probably be the lowest amount of heat needed to obtain one mole of the hexahydrate crystals from a two molar solution of magnesium chloride. Figure 11 illustrates a process

Figure 11. Magnesium hydroxide system: processing scheme.

flowsheet for this case except that the hexahydrate crystals would go directly from the evaporator to the dehydrator. No saturated magnesium chloride solution would be recycled.

After obtaining these hydrated crystals, additional water must be removed before the chloride can be reacted at high temperature to produce hydrogen chloride. Kelley (36) has reported the heat requirements for these dehydration steps. At 450°K, the dihydrate can be obtained from the hexahydrate but the reaction has a high heat requirement of 252. kJ/mole.

Further dehydration at higher temperature will result in significant formation of hydrogen chloride and the hydroxychloride;

The magnesium hydroxychloride will then further decompose to release hydrogen chloride and form the oxide of magnesium;

A number of processes have been proposed or are used which produce magnesium oxide from hydrated crystals of magnesium chloride. The methods used in these processes include spray drying against a flow of superheated steam (51, 56) and fluidized bed reactors (25, 40). The heat requirement for these processes is quite high. An input of + 148.3 kJ/mole is needed to obtain anhydrous magnesium chloride from the dihydrate, while approximately + 91.9 kJ/mole is required to form the oxide. These two reactions would most probably be carried out in the same reactor with the dihydrate being fed countercurrent against the steam.

The total process energy required is obviously seriously inflated by the high heat of evaporation and dehydration needed to obtain the dihydrate from solution. A total estimate of 581.9 kJ/mole is arrived at for the energy needed. This figure does not include any consideration for imperfect heat exchange or mixing or pumping work. Handling of the solid component would make it difficult to conserve heat effectively.

The enthalpy changes listed in the above reactions will not sum to the enthalpy change of the reverse Deacon reaction because of the large amount of water (26.38 moles) which must be vaporized. By taking the heat of condensation into account the system will sum to give a value close to the enthalpy change expected. These calculations have been included in Appendix IV, listed as reaction 25-32.

The magnesium hydroxide reaction system is inefficient because of the large amount of heat liberated by the chlorination step. This waste heat is rejected at a low temperature (less than 373°K) therefore cannot serve any useful purpose. Only if a more concentrated solution could be obtained, yielding a lower hydrated form of magnesium chloride could a more favorable process be developed.

Case II

As shown earlier (Table 1) a dihydrate of magnesium chloride is in equilibrium with a saturated solution at greater than 181°C and hence elevated pressure. If under these conditions the chlorination reaction could be operated in a concentrated solution a much more

favorable reaction system could be developed. This system would involve the following reactions;

In the first reaction oxygen is liberated as before but in a concentrated solution of magnesium chloride. The dihydrate of the chloride is crystallized from solution as the reaction proceeds. Wentorf and Hanneman (64) reported that less heat would be liberated by the chlorination reaction if lower hydrates were to form. Thermodynamic calculations support this claim and as the above reaction shows, a lower amount of heat, 67.35 kJ/mole (15.95 kcal/mole) would be released if a dihydrate would form as a product.

The process diagram, Figure 11, would be altered for this reaction system because no evaporation or dehydration would be needed. A saturated magnesium chloride solution would be returned to a reactor operated at elevated temperature and pressure. Reaction of the dihydrate with steam to produce hydrogen chloride would be the same as in the first case with a total requirement of + 240.2 kJ/mole (57.4 kcal/mole). Again this figure is optimistic for it neglects consideration of the imperfect heat recovery from the solids product. Hypothesizing that this latest heat can be recovered with an efficiency of 50% would add approximately 37. kJ/mole (9 kcal/mole) to the overall process

requirement. The total energy needed would thus be about 277 kJ/mole Cl_2 reacted (66 kcal/mole). Although this figure is quite high it is not too much greater than the estimate for the reverse Deacon reaction if separation processes of low efficiency must be used.

The estimate of 277 kJ/mole also assumes no separation work is needed to obtain a pure stream of oxygen from the chlorination reaction. Experimental investigation is needed, first, to confirm the feasibility of operating the reaction at elevated temperature and pressure to obtain a dihydrate, and, second, to study the composition of the exiting gas under such conditions.

Magnesium Oxide Reaction System

A simple reaction system which could be used to replace the reverse Deacon reaction is given by;

which was proposed by Abraham and Schreiner (1) to replace the magnesium hydroxide reaction system. The second reaction is obviously the same as that used in the magnesium hydroxide system, except that the magnesium chloride is anhydrous and no heat is required for dehydration. The conversion for this endothermic reaction is graphed as a function of temperature in Figure 12. The curve shows a favorable equilibrium at higher temperatures.

Figure 12. Anhydrous magnesium chloride reaction with steam (stoichiometric feed of reactants, total pressure 1 atmosphere).

The reaction between chlorine and magnesium oxide has favorable thermodynamics at low temperatures, but no experimental confirmation of the feasibility of the reaction could be found in the literature. Ino and Ochiai (33) reported that poor results were obtained at 673°K but no operating pressure was mentioned. Figure 13 shows how the theoretical conversion depends on temperature and pressure. If high temperatures are needed to give favorable kinetics, operating at higher pressure will insure a favorable yield.

The thermodynamic data are listed in Appendix IV for reactions 2 and 3. The reaction which produces oxygen liberates approximately 36.2 kJ/mole (8.66 kcal/mole) at 600°K, while that which produces hydrogen chloride requires 92.0 kJ/mole (21.9 kcal/mole).

An attractive method of operating these reactions involves contacting the gases with the magnesium compounds held in fixed beds. Figure 14 illustrates how this would benefit the system. In Case I chlorine at high pressure could be fed to a bed of magnesium oxide. A reaction boundary would develop where complete conversion would be approached on the upstream side of the bed. Theoretically the exit gas could be pure oxygen. In Case II the flow is reversed in the same tube only the feed for this reactor would be steam at high temperature. The same principle applies this time, with the effluent gas being pure hydrogen chloride gas. The fixed beds used could be mounted as tubes in a shell and tube heat exchanger to handle the heat requirements. This proposal benefits from the fact that no solid compounds need to be transferred and heat can be better exchanged. Pure streams of the product gases can be obtained and no separation work is needed.

Figure 13. Magnesium oxide reaction with chlorine (stoichiometric feed).

Figure 14. Reaction system using fixed beds of magnesium compounds.

If the chlorination reaction is performed under conditions of high temperature, the heat released can be used elsewhere in the process.

Before such a system could be employed, however, experimental confirmation is needed. An article published in the Ukrainian Chemical Journal (58) describes a process in which magnesium compounds are used to catalyze the reverse Deacon reaction. The reaction between magnesium chloride and steam forms the intermediate Mg(OH)Cl , as reported earlier, which will decompose to release additional hydrogen chloride. However, if operating alternating fixed bed reactors the hydroxychloride may not be completely decomposed. Contacting chlorine with the bed will then give the following reaction;

Thus a complete conversion to oxygen may not be realized, and hydrogen chloride will be present in the exiting stream of oxygen. An equilibrium diagram for the $\text{MgO-HCl-H}_2\text{O}$ system (60) shows no Mg(OH)Cl present provided the temperature is above 850°K and the mole fraction of HCl in the gas phase is less than 50%.

This system appears to have the potential of requiring less energy than the reverse Deacon reaction because it could hopefully avoid any separation work. Ideally the total energy requirement would be only that needed for the enthalpy change of the magnesium chloride steam reaction. Thus a total requirement of 92.0 kJ/mole Cl_2 reacted could be anticipated. This alternative also benefits for it provides 36.2 kJ/mole as heat at 600°K which might be used by other requirements of the thermochemical system.

Other Reaction Systems

The thermodynamics of five other systems were examined to see if a better alternative might be available to replace the reverse Deacon reaction. These alternatives include four reaction systems which replace magnesium with other alkali earth metals. The proposed reactions and the values of the thermodynamic constants for these systems are listed in Appendix IV. Metals examined include calcium (reactions 8-11), sodium (reactions 12-15), potassium (reactions 16-19), and beryllium (reactions 20-22). Of these systems none had thermodynamic constants more favorable than the magnesium compound reactions. In most cases the metal chloride will not react with steam to give an appreciable yield of hydrogen chloride. With beryllium, however, the reaction to liberate oxygen has an associated large free energy of reaction.

A final alternative proposes the use of compounds of copper in a system similar to that of the magnesium oxide fixed bed reactor. The results listed in Appendix IV (reactions 23 and 24) show the unfavorable thermodynamics calculated for the reactions. Although copper chloride is a catalyst used in the reverse Deacon reaction, it does not appear feasible to operate the reactions separately.

CONCLUSIONS AND RECOMMENDATIONS

1. Magnesium hydroxide will react with chlorine to yield oxygen and magnesium chloride. The reaction occurs readily in a dilute solution of magnesium chloride with cobalt oxide present as a catalyst. The reaction proceeds in two steps, the first being the formation of the hypochlorite in the slightly alkaline solution. The second step is the catalyzed decomposition of the hypochlorite to release oxygen and form chloride ions. In the experiments performed, absorption of chlorine in solution appeared to be rate controlling.

2. The reaction between chlorine and magnesium hydroxide will not occur in a concentrated magnesium chloride solution. No conditions are known which might allow for crystals of magnesium chloride hydrates to form as the reaction proceeds.

3. The heat and work requirements of the reverse Deacon process were compared with those of three alternative systems. The results are summarized in Table 9.

Only the magnesium oxide system had a lower total heat requirement than the reverse Deacon process. Those systems which react magnesium hydroxide with chlorine in a solution all have much greater energy requirements primarily because of the large amount of heat needed to obtain anhydrous magnesium chloride from the solution.

The relative efficiency listed is simply the ratio of the enthalpy change of the reverse Deacon reaction to the estimated heat required for the various processes. Since these figures are "relative" to the reverse Deacon reaction they are not a true measure of how efficient

Table 9. Heat and work requirements for the different processes

System	Estimated heat requirement (kJ)	Relative efficiency ^a (%)
A. Reverse Deacon process	Between 115. and 210. kJ	27.5 and 50.3
B. Mg(OH) ₂ system in weak (2M MgCl ₂) solution	581.9	9.9
C. Mg(OH) ₂ reaction in conc. solution with dihydrate crystals forming	277.	20.8
D. MgO system - fixed bed	92.0	62.9

^aRelative to the heat of reaction (57.86 kJ) for the reverse Deacon reaction.

the systems would be in various thermochemical cycles. A knowledge of the entire thermochemical process is needed before a complete analysis of the efficiency can be made.

For example, a particular cycle may have a reaction which liberates heat at a high temperature. If a portion of this heat could be used to dehydrate magnesium chloride crystals the magnesium hydroxide systems would appear more favorable. However, this increase in efficiency obviously comes only at the expense of another exothermic reaction. Any thermochemical cycle which provides enough "waste" heat to dehydrate the magnesium chloride crystals is probably already an inefficient process. Of the thermochemical cycles which use the reverse Deacon reaction the most efficient would be that which has no large amount of associated waste heat and uses the best method of performing this oxygen liberating step.

4. The magnesium oxide system has potential for efficiency better than the reverse Deacon reaction. Research is needed to confirm the possibility of operating the reactions in fixed beds, and in studying the major process parameters. The reaction system will only have an advantage if no separation work is required.

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ACKNOWLEDGMENT

The author would like to express thanks to Dr. Dean L. Ulrichson for the helpful council throughout this study.

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

1. R. H. Wentorf, Jr., and R. E. Hanneman, Process A - Agnes (64)

	<u>Temperature °C</u>
$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	450-900
$\text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$	50-110
$2\text{FeCl}_3 \rightarrow 2\text{FeCl}_2 + \text{Cl}_2$	300
$\text{Cl}_2 + \text{Mg}(\text{OH})_2 \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$	50-90
$\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{HCl}$	350

2. R. H. Wentorf, Jr., and R. E. Hanneman, Process B (64)

	<u>Temperature °C</u>
$2\text{Cu} + 2\text{HCl} \rightarrow 2\text{CuCl} + \text{H}_2$	100
$4\text{CuCl} \rightarrow 2\text{CuCl}_2 + 2\text{Cu}$	30-100
$2\text{CuCl}_2 \rightarrow 2\text{CuCl} + \text{Cl}_2$	500-600
$\text{Mg}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} - \frac{1}{2} \text{O}_2$	80
$\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{HCl}$	350

3. Funk and Reinstrom, Vanadium Chloride Process (20)

	<u>Temperature °C</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	700
$2\text{HCl} + 2\text{VCl}_2 \rightarrow 2\text{VCl}_3 + \text{H}_2$	25
$4\text{VCl}_3 \rightarrow 2\text{VCl}_4 + 2\text{VCl}_2$	700
$2\text{VCl}_4 \rightarrow 2\text{VCl}_3 + \text{Cl}_2$	25

4. Hardy; Euratom, Mark 7 (32)

	<u>Temperature °C</u>
$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	650
$\text{Fe}_3\text{O}_4 + \frac{1}{4} \text{O}_2 \rightarrow \frac{3}{2} \text{Fe}_2\text{O}_3$	350
$\frac{3}{2} \text{Fe}_2\text{O}_3 + 9\text{HCl} \rightarrow 3\text{FeCl}_3 + \frac{9}{2} \text{H}_2\text{O}$	150
$3\text{FeCl}_3 \rightarrow 3\text{FeCl}_2 + \frac{3}{2} \text{Cl}_2$	420
$\frac{3}{2} \text{H}_2\text{O} + \frac{3}{2} \text{Cl}_2 \rightarrow 3\text{HCl} + \frac{3}{2} \text{O}_2$	800

5. DeBeni, Euratom (32)

	<u>Temperature °C</u>
$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	800
$2\text{HCl} + 2\text{CrCl}_2 \rightarrow 2\text{CrCl}_3 + \text{H}_2$	170
$2\text{CrCl}_3 + 2\text{FeCl}_2 \rightarrow 2\text{CrCl}_2 + 2\text{FeCl}_3$	700
$2\text{FeCl}_3 + 2\text{CuCl} \rightarrow 2\text{FeCl}_2 + 2\text{CuCl}_2$	150
$2\text{CuCl}_2 \rightarrow 2\text{CuCl} + \text{Cl}_2$	500

6. K. F. Knoche, H. Cremer, G. Steinborn, 1975, Iron Chloride

Process (10)

	<u>Temperature °K</u>
$3\text{FeCl}_2 + 3\text{H}_2 \rightarrow 6\text{HCl} + 3\text{Fe}$	1300
$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$	600
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	700
$\frac{1}{2} \text{Cl}_2 + \text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow \frac{3}{2} \text{Fe}_2\text{Cl}_6 + 4\text{H}_2\text{O}$	1300
$\frac{3}{2} \text{Fe}_2\text{Cl}_6 \rightarrow 3\text{FeCl}_2 + \frac{3}{2} \text{Cl}_2$	600

7. K. F. Knoche, Julich (1972), Chromium Chloride Process (10)

8. G. DeBeni, Mark 3 (32)

9. C. Hardy, Mark 4 (32)

APPENDIX II. THERMOCHEMICAL CYCLES - EXAMPLES WHICH
DO NOT EMPLOY REVERSE DEACON REACTION

1. C. Hardy, Mark 9 (32)

	<u>Temperature °K</u>
$6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2$	923
$2\text{Fe}_3\text{O}_4 + 3\text{Cl}_2 + 12\text{HCl} \rightarrow 6\text{FeCl}_3 + 6\text{H}_2\text{O} + \text{O}_2$	423-473
$6\text{FeCl}_3 \rightarrow 6\text{FeCl}_2 + 3\text{Cl}_2$	693

2. G. DeBeni, Mark 8 (32)

	<u>Temperature °K</u>
$6\text{MnCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Mn}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2$	973
$3\text{MnO} + 12\text{HCl} \rightarrow 6\text{MnCl}_2 + 3\text{MnO}_2 + 6\text{H}_2\text{O}$	373
$3\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 + \text{O}_2$	1173

3. R. H. Wentorf and R. E. Hanneman (64)

	<u>Temperature °K</u>
$3\text{I}_2 + 6\text{LiOH} \rightarrow 5\text{LiI} + \text{LiIO}_3 + 3\text{H}_2\text{O}$	373
$\text{LiIO}_3 + \text{KI} \rightarrow \text{KIO}_3 + \text{LiI}$	273
$\text{KIO}_3 \rightarrow \text{KI} + \frac{3}{2} \text{O}_2$	923
$6\text{LiI} + 6\text{H}_2\text{O} \rightarrow 6\text{HI} + 6\text{LiOH}$	723-873
$6\text{HI} + 3\text{Ni} \rightarrow 3\text{NiI}_2 + 3\text{H}_2$	423
$3\text{NiI}_2 \rightarrow 3\text{Ni} + 3\text{I}_2$	973

4. VonFredersdorf, 1GT (21)

	<u>Temperature</u>
$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2$	823+
$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	823+
$\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$	823+
$2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$	(Chemonuclear reactor)

5. DeBeni, Mark 1 (10, 32)

	<u>Temperature °K</u>
$\text{CaBr}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HBr}$	1003
$\text{Hg} + 2\text{HBr} \rightarrow \text{HgBr}_2 + \text{H}_2$	423
$\text{HgBr}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$	473
$\text{HgO} \rightarrow \text{Hg} + \frac{1}{2} \text{O}_2$	873

APPENDIX III. COMBINED THERMOCHEMICAL-ELECTROLYTIC PROCESSES (54)

1. Hydrogen chloride electrolytic process

Temperature °K

973

(Electrolysis)

2. Mercury chloride process

Temperature °K

973

573

(Electrolysis)

3. Iron chloride electrolysis process

Temperature °K

973

(Electrolysis)

448

423

4. Copper chloride electrolytic process

Temperature °K

973

(Electrolysis)

573

APPENDIX IV. THERMODYNAMIC CONSTANTS (5, 34, 36)

Reaction	Temperature (°K)	ΔH (kJ/mole)	ΔG (kJ/mole)
1) $\text{H}_2\text{O}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	300	+ 57.86	+ 38.53
	400	+ 58.28	+ 32.00
	500	+ 58.62	+ 25.40
	600	+ 58.87	+ 18.74
	700	+ 59.08	+ 12.05
	800	+ 59.29	+ 5.31
	900	+ 59.50	- 1.46
	1000	+ 59.71	- 8.24
	1100	+ 59.87	- 15.06
2) $\text{MgO}(\text{c}) + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{c}) + \frac{1}{2} \text{O}_2(\text{g})$	298	- 40.17	- 22.59
	400	- 38.74	- 17.19
	500	- 37.49	- 11.96
	600	- 36.2	- 6.99
	700	- 35.02	- 2.21
	800	- 33.76	+ 2.38
	900	- 32.46	+ 6.82

Reaction	Temperature (°K)	ΔH (kJ/mole)	ΔG (kJ/mole)
3) $\text{MgCl}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{MgO}(\text{c}) + 2\text{HCl}(\text{g})$	298	+ 97.99	+ 61.54
	400	+ 97.03	+ 49.24
	500	+ 96.11	+ 37.40
	600	+ 94.98	+ 25.77
	700	+ 94.10	+ 14.27
	800	+ 93.09	+ 2.94
	900	+ 92.00	- 8.26
4) $\text{Mg}(\text{OH})_2(\text{c}) + \text{Cl}_2(\text{g}) \rightarrow \text{MgCl}_2(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	298	- 158.07	- 121.84
5) $\text{MgCl}_2(\text{aq}) \rightarrow \text{MgCl}_2(\text{c})$	298	+ 155.06	+ 126.00
6) $\text{MgCl}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{MgO}(\text{c})$	900	+ 91.96	- 8.26
7) $\text{MgO}(\text{c}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{c})$	298	- 37.57	- 27.49
<u>Sum</u> $\text{H}_2\text{O}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \frac{1}{2} \text{O}_2(\text{g}) + 2\text{HCl}(\text{g})$		51.41	
8) $\text{Ca}(\text{OH})_2(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	298	- 160.91	- 184.89
9) $\text{CaCl}_2(\text{aq}) \rightarrow \text{CaCl}_2(\text{c})$	298	+ 82.92	+ 65.34
10) $\text{CaCl}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{CaO}(\text{c})$	1000	+ 219.87	+ 116.27
11) $\text{CaO}(\text{c}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$	298	- 81.42	- 26.03
<u>Sum</u> $\text{H}_2\text{O}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \frac{1}{2} \text{O}_2(\text{g}) + 2\text{HCl}(\text{g})$		+ 60.46	

Reaction	Temperature (°K)	ΔH (kJ/mole)	ΔG (kJ/mole)
12) $2\text{NaOH}_{(\text{aq})} + \text{Cl}_{2(\text{g})} \rightarrow 2\text{NaCl}_{(\text{aq})} + \frac{1}{2} \text{O}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	298	- 161.00	- 185.10
13) $2\text{NaCl}_{(\text{aq})} \rightarrow 2\text{NaCl}_{(\text{c})}$	298	- 7.75	+ 17.92
14) $2\text{NaCl}_{(\text{c})} + \text{H}_2\text{O}_{(\text{g})} \rightarrow 2\text{HCl}_{(\text{g})} + \text{Na}_2\text{O}_{(\text{c})}$	1000	+ 458.61	+ 348.95
15) $\text{Na}_2\text{O}_{(\text{c})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{NaOH}_{(\text{aq})}$	298	- 237.48	- 250.35
<u>Sum</u> $\text{H}_2\text{O}_{(\text{g})} + \text{Cl}_{2(\text{g})} \rightarrow \frac{1}{2} \text{O}_{2(\text{g})} + 2\text{HCl}_{(\text{g})}$		52.37	
16) $2\text{KOH}_{(\text{aq})} + \text{Cl}_{2(\text{g})} \rightarrow 2\text{KCl}_{(\text{aq})} + \frac{1}{2} \text{O}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	298	- 160.83	- 184.94
17) $2\text{KCl}_{(\text{aq})} \rightarrow 2\text{KCl}_{(\text{c})}$		- 34.48	+ 10.260
18) $2\text{KCl}_{(\text{c})} + \text{H}_2\text{O}_{(\text{g})} \rightarrow \text{K}_2\text{O}_{(\text{c})} + 2\text{HCl}_{(\text{g})}$	1000	+ 572.58	+ 450.53
19) $\text{K}_2\text{O}_{(\text{c})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{KOH}_{(\text{aq})}$		- 314.97	
<u>Sum</u> $\text{H}_2\text{O}_{(\text{g})} + \text{Cl}_{2(\text{g})} \rightarrow \frac{1}{2} \text{O}_{2(\text{g})} + 2\text{HCl}_{(\text{g})}$		+ 62.30	
20) $\text{Be}(\text{OH})_{2(\text{c})} + \text{Cl}_{2(\text{g})} \rightarrow \text{BeCl}_{2(\text{c})} + \frac{1}{2} \text{O}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	300	+ 120.7	+ 127.82
21) $\text{BeCl}_{2(\text{c})} + \text{H}_2\text{O}_{(\text{g})} \rightarrow 2\text{HCl}_{(\text{g})} + \text{BeO}_{(\text{c})}$	300	- 44.68	- 81.51
22) $\text{BeO}_{(\text{c})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Be}(\text{OH})_{2(\text{c})}$	300	- 18.15	- 7.68
<u>Sum</u> $\text{H}_2\text{O}_{(\text{g})} + \text{Cl}_{2(\text{g})} \rightarrow 2\text{HCl}_{(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})}$		57.87	

Reaction	Temperature (°K)	ΔH (kJ/mole)	ΔG (kJ/mole)
23) $\text{Cu}_2\text{O}_{(c)} + \text{Cl}_{2(g)} \rightarrow 2\text{CuCl}_{(c)} + \frac{1}{2} \text{O}_{2(g)}$	298	- 105.85	- 94.123
	400	- 104.36	- 90.323
	500	- 102.55	- 87.02
	600	- 100.35	- 84.123
	700	- 97.725	- 81.611
24) $2\text{CuCl}_{(c)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Cu}_2\text{O}_{(c)} + 2\text{HCl}_{(g)}$	298	+ 163.69	+ 132.78
	400	+ 162.66	+ 122.35
	500	+ 161.17	+ 112.44
	600	+ 159.22	+ 102.86
	700	+ 156.828	+ 93.65
25) $\text{Mg}(\text{OH})_{2(c)} + \text{Cl}_{2(g)} \rightarrow \text{MgCl}_{2(c)} + \text{H}_2\text{O}_{(l)} + \frac{1}{2} \text{O}_{2(g)}$	298	- 2.59	
26) $\text{MgCl}_{2(c)} \rightarrow \text{MgCl}_{2(aq)}$	298	- 156.73	
27) $6\text{H}_2\text{O}_{(l)} + \text{MgCl}_{2(aq)} \rightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}_{(c)}$	298	+ 12.38	
28) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}_{(c)} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O}_{(c)} + 2\text{H}_2\text{O}_{(g)}$	298	+ 252.00	
29) $\text{MgCl}_2 \cdot \text{H}_2\text{O}_{(c)} \rightarrow \text{MgCl}_{2(c)} + \text{H}_2\text{O}_{(g)}$	298	+ 148.32	
30) $\text{MgCl}_{2(c)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{MgO}_{(c)} + 2\text{HCl}_{(g)}$	800	97.90	

Reaction	Temperature (°K)	ΔH (kJ/mole)	ΔG (kJ/mole)
31) $\text{MgO}_{(c)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Mg}(\text{OH})_{2(c)}$	298	- 37.57	
32) $6\text{H}_2\text{O}_{(g)} \rightarrow 6\text{H}_2\text{O}_{(l)} \rightarrow$	298	<u>- 264.09</u>	
<u>Sum</u> $\text{H}_2\text{O}_{(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)} + \frac{1}{2} \text{O}_{2(g)}$	.	+ 49.62	

APPENDIX V. EXPERIMENTAL HISTORY

Experiment No.	Conditions			Comments
	Temp.	Mg(OH) ₂	Catalyst	
I	50°C	0.10 moles	None	Familiarization with system, problems encountered controlling Cl ₂ flow.
II	50°C	0.01	None	Mg(OH) ₂ reacted completely, hypochlorite produced.
III	50°C	0.02 moles NaOH	None	NaOH reacted completely, hypochlorite produced, no oxygen liberated.
IV	50°C	0.10 moles	None	Chlorine added to system for 30 min @ 20 cc/min. Addition of cobalt chloride-liberated small amount of oxygen.
V	50°C	0.10 moles	0.40 gm CoCl ₂	Chlorine flow monitored as a function of gas collected.
VI	50°C	0.01 moles	0.40 gm CoCl ₂	Mg(OH) ₂ reacted to completion. Chloride ion concentration measured and correspond with total conversion to chloride.
VII	50°C	0.10 moles	0.40 gm NiCl ₂	Molar flow of chlorine approximately twice the rate oxygen exited the system.
VIII	50°C	None	0.40 gm CoCl ₂	No cobalt oxide produced.
IX	50°C	None	0.40 gm NiCl ₂	No nickel oxide produced.
X	50°C	0.10 mole	0.40 gm CoCl ₂	Gas flow rate monitored.
XI	50°C	0.054 mole	Excess CoCl ₂	Cobalt oxide sample prepared for X-ray diffraction test.
XII	50°C	0.10 mole	0.258 gm Co ₂ O ₃	Test effect of recycling dried catalyst.

Experiment No.	Conditions			Comments
	Temp.	Mg(OH) ₂	Catalyst	
XIII	50°C	0.10 mole	None	Test to measure the maximum flow of chlorine which could be absorbed, found to be 50 cc/min.
XIV A	50°C	0.10	0.40 gm CoCl ₂	Series of experiments to determine the effect of different catalyst concentration. In each experiment the gas flows of chlorine in and oxygen exiting were recorded. Total volume of oxygen was recorded. Mg(OH) ₂ was reached to completion in Experiments F-J.
B	50°C	0.10	0.20 gm CoCl ₂	
C	50°C	0.10	0.04 gm CoCl ₂	
D	50°C	0.10	0.04 gm CoCl ₂	
E	50°C	0.10	0.08 gm CoCl ₂	
F	50°C	0.10	0.04 gm CoCl ₂	
G	50°C	0.10	0.04 gm CoCl ₂	
H	50°C	0.10	0.04 gm CoCl ₂	
I	50°C	0.10	0.04 gm CoCl ₂	
J	50°C	0.10	0.008 gm CoCl ₂	
XVII	50°C	0.10	0.004 gm CoCl ₂	
XV A	50°C	0.10	Recycled 0.04	Effect of allowing catalyst to settle out of solution measured.
XVIII	50°C	0.10	None	Gas exiting measured with no catalyst. Measured hypochlorite, chloride ratio; one to one.
XXI	50°C	20 gm	0.40 gm CoCl ₂	Solution measured for chlorate, chloride and hypochlorite.
XXII	70°C	20 gm	0.40 gm CoCl ₂	Solution measured for chlorate, chloride and hypochlorite.

Experiment No.	Conditions			Comments
	Temp.	Mg(OH) ₂	Catalyst	
XXIII	80°C	20 gm	0.40 gm	Solution measured for chlorate, chloride and hypochlorite.
XXIV	80°C	20 gm	0.40 gm	Solution measured for chlorate, chloride and hypochlorite.
XXV	50°C	20 gm	0.40 gm CoCl ₂	Total ions measured, inconsistent result obtained in measuring low chlorate concentration.
XXVI	65°C	20 gm	0.40 gm CoCl ₂	Total ions measured, inconsistent result obtained in measuring low chlorate concentration.
XXVII	72°C	10 gm	0.40 gm CoCl ₂	Total ions measured, inconsistent result obtained in measuring low chlorate concentration.
XXVIII	80°C	10 gm	0.74 gm CoCl ₂ • 6H ₂ O	Reaction attempted in a concentrated solution of MgCl ₂ . No reaction observed.