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ACTION OF MANGANESE AND RHENIUM COMPOUNDS IN THE DECOMPOSITION OF POTASSIUM CHLORATE

by

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Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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The legends on illustrations in this thesis are unsatisfactory. Candidates are warned that theses with similar untidy figures will be rejected.--R.M.H.

Iowa State College
1954

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TABLE OF CONTENTS

INTRODUCTION

Literature Survey

In 1832 Dobereiner (1) first reported that potassium chlorate can be readily decomposed if it is mixed with pyrolusite. The story of this and other events in Dobereiner's life are told by Prandt (2).

Since Dobereiner's discovery many researchers have reported results of investigations of the decomposition of potassium chlorate, with and without catalytic agents. Following is a somewhat chronological account of the significant studies in the literature.

McLeod (3) studied the action of MnO_2 on the decomposition of $KClO_3$ and reported that chlorine could be detected in the evolved oxygen. He also observed a pink color in the mixture when very small amounts of MnO_2 were used as catalysts. Finding that $KMnO_4$ also has a catalytic effect on the decomposition, he proposed the following reactions for the catalysis:

$$\text{I.} \quad 2MnO_2 + 2KClO_3 \longrightarrow K_2Mn_2O_8 + Cl_2 + O_2$$

$$\text{II.} \quad K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

Brunch (4) disagreed with McLeod's claim that chlorine could be detected in the oxygen evolved during the decomposition of $KClO_3$. He ascribed extra oxidizing power of the oxygen to a trace of ozone.

McLeod (5) later reported more conclusive evidence that chlorine was liberated with oxygen when potassium chlorate is decomposed with MnO_2. Hodgkinson and Lowndes (6) also detected chlorine in oxygen liberated from $KClO_3$ with MnO_2.

Sodeau (7) studied the decomposition of $Ba(ClO_3)_2$ and of $KClO_3$ and concluded that when $KClO_3$ decomposes, it undergoes two reactions: one, into chloride and oxygen; and two, into oxide, chlorine, and oxygen. Sodeau (8) also used MnO_2 as a catalyst and agreed with McLeod that chlorine was evolved with the oxygen. However, he did not agree that the liberated chlorine was a part of the cycle of changes bringing about the decomposition of the chlorate. He believed, however, that the catalysis involved the oxidation of manganese by the chlorate and the subsequent breaking up of the higher oxide.

Fowler and Grant (9) studied the effect of a variety of oxides on the decomposition of potassium chlorate. They found that acidic oxides such as V_2O_5, U_3O_8, and WO_3 evolved oxygen plus chlorine, and formed the vanadate, uranate and tungstate. More basic oxides such as Fe_2O_3, Co_2O_3, NiO, CuO, and MnO_2 yielded oxygen and no chlorine, leaving the oxides unchanged. They pointed out that water of hydration in the oxides could have an effect on the activities of the catalysts. They proposed a possible mechanism of the decomposition when MnO_2 was used as a catalyst, according to the following unbalanced equations:

$$MnO_2 + O + K_2O \longrightarrow KMnO_4$$

$$KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O$$

$$K_2MnO_4 + Cl \longrightarrow KCl + MnO_2$$

It is significant that $KMnO_4$ was a proposed intermediate. However, evidence for it was not cited. No proposed mechanism for the other oxides was given. Fowler and Grant also reported that the addition of sodium carbonate to potassium chlorate retarded the normal evolution of oxygen when chlorate was decomposed.

Deniges (10) found spectroscopic evidence for the formation of manganese permanganate in the course of the decomposition of $KClO_3$ with MnO_2. He stated that $KMnO_4$ dissolved in molten $KClO_3$ without immediate signs of decomposition at temperatures above the decomposition temperature of mixtures of $KClO_3$ and MnO_2. Though believing that small amounts of $KMnO_4$ might be formed in the catalysis, Deniges assumed that it was $Mn(MnO_4)_2$ which formed and decomposed according to the following reactions:

$$\text{I.}\quad 9MnO_2 + 2KClO_3 \longrightarrow 3Mn(MnO_4)_2 + 2KCl$$

$$\text{II.}\quad 3Mn(MnO_4)_2 \longrightarrow 9MnO_2 + 3O_2$$

No concrete evidence was shown for this proposal, however.

Kolhatker and Sant (11) later carried out a comparison of the catalytic activities of several oxides toward decomposition of $KClO_3$. They listed in the order of decreasing activity the following: Co_2O_3, Cr_2O_3, MnO_2, Fe_2O_3, Ni_2O_3, and CuO. They compared the activities by volumetrically measuring the rates of oxygen evolution.

Brown and co-workers (12,13) showed that when homogeneous mixtures of potassium chlorate and MnO_2 or Fe_2O_3 are heated rapidly, those mixtures containing fairly large amounts of catalysts have a characteristic spontaneous decomposition temperature.

Neville (14) showed that Fe_2O_3 promotes MnO_2, and MnO_2 promotes Fe_2O_3 in the catalytic decomposition of $KClO_3$. Burrows and Brown (15), however, reported that the addition of MnO_2 to Fe_2O_3 as catalyst lowered the spontaneous decomposition of the chlorate mixture, not because of promotor action but simply because MnO_2 is a better catalyst than Fe_2O_3.

McLaughlin and Brown (16) showed that pressure has a definite effect on the decomposition of potassium chlorate. The decomposition of potassium chlorate in the presence of manganese dioxide was retarded by pressures of oxygen below 500 atmospheres when mixtures were heated for periods of several hours at temperatures 40° above the normal spontaneous decomposition temperatures of the mixtures. They also believed that water had a promotor effect on the activity of the catalyst.

Barlereff (17) reported that water had no definite effect on heating curves of MnO_2 - $KClO_3$ systems. He also stated that no definite temperature was found for the catalytic action of MnO_2 in the decomposition of $KClO_3$. He further stated that the decomposition temperature of potassium chlorate without MnO_2 is much less than 230°-280° C.

Mathers and Alred (18) heated pure potassium chlorate under various conditions of temperature, time of heating, and size of sample. They found that the best yield of perchlorate in the residues was about 55%. Glass, Ag_2O, Pb_3O_4, and HgO all lowered the yield of perchlorate.

Otto and Fry (19,20) carried out kinetic studies on the thermal decomposition of both pure potassium perchlorate and potassium chlorate. They concluded that decomposition of potassium chlorate itself is not simple, but involves two simultaneous reactions:

$$\text{I.}\quad 2KClO_3 \longrightarrow 2KCl + 3O_2$$

$$\text{II.}\quad 4KClO_3 \longrightarrow 3KClO_4 + KCl$$

At higher temperatures $KClO_4$ also decomposes:

$$\text{III.}\quad KClO_4 \longrightarrow KCl + 2O_2$$

Otto and Fry further showed that reactions I and III are unimolecular. The reaction becomes complicated, however, by the fact that KCl catalyzes reaction II. It is significant that Otto and Fry, working with pure reagents, found no chlorine liberated with oxygen when potassium chlorate was decomposed with or without an MnO_2 catalyst. They assumed that the earlier workers probably observed chlorine which was liberated because of impure chlorate.

Farmer and Firth (21) report results of kinetic studies which also show that KCl catalyzes the formation of $KClO_4$. Their data differ from that of Otto and Fry, however. They found that KCl increased both the rate of oxygen evolution and of perchlorate formation, whereas Otto and Fry found that KCl decreased the amount of oxygen evolved in a given time.

The more recent literature sheds more light on the nature of the decomposition of potassium chlorate, although differences in conclusions are still noted. Glasner amd Weidenfeld (22,23) carried out kinetic studies on the thermal decomposition of potassium chlorate and of potassium perchlorate, including studies on the effect of addition of chloride and bromide as catalysts. They conclude that the mechanism of the decomposition of potassium chlorate involves two consecutive reactions involving an equilibrium in which oxygen is added to chloride:

$$\text{I.}\quad KClO_3 \longrightarrow KCl + 3O$$

$$\text{II.}\quad KCl + 4O \rightleftharpoons KClO_4$$

This conclusion is quite contrary to that of Otto and Fry (20). DeCoursey (24), by oxidizing chlorate to perchlorate with potassium bromate, concludes that it would be more reasonable for the second reaction to occur as follows:

$$KClO_3 + O \rightleftharpoons KClO_4$$

While the present study was in progress, Vanden Bosch and Aten (25) decomposed sodium chlorate in the presence of sodium chloride containing Cl^{34} and Cl^{38}. They found negligible activity in perchlorate from the residue, thus also discrediting the conclusion of Glasner and Weidenfeld.

Bircumsbau and Phillips (26) recently studied the kinetics of thermal decomposition of $KClO_4$. They tried to apply the theories of Prout and Thomkins (27) on kinetics of decomposition of solids. Their reproducibility was so poor that they concluded that application of theories derived for decomposition of solids would hardly apply if melting occurred. Glasner and Weidenfeld (23) found little change in the kinetics below or above the melting point when potassium chlorate decomposed.

Polyakov and Nosenko (28) state that the velocity of decomposition of $KClO_3$ with manganese dioxide depends on the ratio of catalyst to $KClO_3$. They further conclude that the decomposition of $KClO_3$ is not complete at constant temperature, but that completeness of the reaction depends upon the temperature and composition of the mixture.

A very significant recent study by Forkushima, Horibe, and Titani (29) has shed further light on the action of MnO_2 in the catalytic decomposition of potassium chlorate. Decomposing $KClO_3$ enriched with O^{18}, and using ordinary MnO_2 as catalyst, they found less enrichment in the evolved oxygen than was present in the chlorate. This showed that some of the oxygen came from the manganese dioxide. Their isotopic measurements were made by determining densities of water formed from the oxygen. This experiment lends support to the earlier theories that manganese is oxidized and de-oxidized in some cyclic process during the catalytic decomposition of potassium chlorate.

In a former study by the author (30) it was shown that when a small amount of MnO_2 or Mn_3O_4 is used as catalyst in the partial decomposition of $KClO_3$, aqueous extracts of the residue exhibit the absorption spectrum of permanganate. Further, when a mixture of $KClO_3$ and MnO_2 containing less than .1% MnO_2 is approximately 30%

decomposed, as much as 3% of the MnO_2 is converted to permanganate. As much as .4% of the Mn_3O_4 is converted to permanganate when a mixture of $KClO_3$ and 20% Mn_3O_4 is approximately 30% decomposed. This study lent evidence in favor of a mechanism involving the formation of permanganate as a possible intermediate in the decomposition of potassium chlorate using MnO_2 or Mn_3O_4.

Discussion and Statement of Problem

The literature shows that the decomposition of potassium chlorate is complex and that the mechanism of the decomposition is in doubt. Otto and Fry (19) proposed that the decomposition involves two simultaneous reactions, the formation of chloride and oxygen, and the disproportionation to chloride and perchlorate. Glasner and Weidenfeld (23) suggested that these reactions are consecutive rather than simultaneous. Since radioactive tracers are now available, a check on which of these two proposals is more feasible can readily be carried out. In fact, during the course of this investigation Vanden Bosch and Aten (25) reported results of such an experiment that discredit the conclusions of Glasner and Weidenfeld. Further study of this reaction using isotopic tracer techniques is appropriate for elucidating more completely the mechanism by which pure potassium chlorate itself decomposes.

Many experiments are reported describing various catalysts for the decomposition of potassium chlorate; however, few mechanisms have been shown for the catalysis involved. Many of the studies involve manganese dioxide as the catalyst. Mangano-manganic oxide (Mn_3O_4) has also been used. The literature search revealed little use of other oxides of manganese as catalysts for this reaction.

The type of cation combined with chlorate has a marked effect on the stability of a particular chlorate compound. Likewise, the mode of decomposition of the chlorate is influenced by the type of cation present. For example, potassium chlorate decomposes to potassium chloride and oxygen. Wachter (31) reported that chromium chlorate decomposes to yield chlorine.

Manganese chlorate is unstable, even in solution, and has not previously been described. Since manganese is a good catalyst for decomposing chlorate, and since manganese chlorate is unstable, it might be reasonable to guess that manganese chlorate is involved as an intermediate in the catalysis when manganese is used to decompose potassium chlorate. The preparation and description of the properties of manganese chlorate is significant for this study.

A former study by the author (30) indicated that permanganate formation accompanies the decomposition of potassium chlorate when either MnO_2 or Mn_3O_4 is used as catalyst. When reaction mixtures were suddenly cooled, permanganate could be extracted from the residues even though the temperatures of the mixtures were far above the decomposition temperature of potassium permanganate.

A study of the decomposition of potassium chlorate, using as catalysts a variety of compounds of manganese in different oxidation states (including $KMnO_4$), should aid in determining if permanganate is an essential to the catalysis. Analysis of any residual oxides should indicate whether the oxidation state of manganese changes during catalysis. Determination of the catalyst that produces the reaction with the lowest activation energy might aid in indicating the path of the reaction.

Activation energies for a reaction can be determined by carrying out the reaction at two or more temperatures and solving for E in the Arrhenius equation (32)

$$\ln k = -\frac{E}{RT} + \text{constant}$$

where E is the activation energy, R is the gas constant, T is the absolute temperature, and k is the specific reaction rate constant. This equation requires that a plot of log k against $\frac{1}{T}$ be a straight line. The k used depends upon the order of the reaction, which must be determined.

For kinetic studies it is desirable to have an accurate and simple method of measuring the rates of the reactions. In a reaction where a gas is evolved, a usual method is to measure the volume or pressure of the gas as a function of time. One also could measure the weight of the residue as a function of time. An instrument with which one could accurately and automatically plot changes of weight as a function of time over extended periods was not formerly available.

In the literature little is made of the periodic family relationships between catalysts and their action toward decomposition of potassium chlorate. In no place has the catalytic activity of rhenium, in the same family as manganese, been described for this reaction.

It is known that the higher oxidation states of the heavier transition elements are more stable than the higher oxidation states of the lighter transition elements. Perrhenate is more stable than permanganate. If oxidation to permanganate and subsequent reduction to a lower oxide is involved in the catalytic decomposition of potassium chlorate, one might predict that rhenium oxides as catalysts would undergo the oxidation half of the cycle. However, due to the stability of perrhenate, the reduction half of the cycle might not take place. Thus, one might expect rhenium compounds to be poorer catalysts than manganese compounds for the catalytic decomposition of potassium chlorate. A later section of this thesis deals with this hypothesis.

A check on the hypothesis that manganese is alternately oxidized and reduced during catalytic decomposition of potassium chlorate can be made by stable isotope tracer techniques. If manganese dioxide were enriched in O^{18} and used to decompose potassium chlorate, the evolved oxygen should contain O^{18} if this mechanism is correct. Forkushima et al (29) have recently published results of such a study in which the O^{18} enrichment was determined by density measurements. Similar experiments using the mass spectrograph for O^{18} determinations are significant for a check on results of this study.

In view of the above discussion, the general purpose of this thesis is to elucidate more fully the catalytic action of manganese compounds on the decomposition of potassium chlorate, to determine if rhenium compounds are also catalysts for this reaction, and to relate the findings for rhenium catalysts to the action of the manganese catalysts.

Specifically, the following objectives for this research were in mind:

1. By use of radiochlorine^{36} tracer to see which of two proposed mechanisms for the decomposition of potassium chlorate is possible.

2. To prepare manganese chlorate and study its properties with a view toward determining if its formation is or is not a part of the catalysis when potassium chlorate is decomposed by manganese catalysts.

3. Through kinetic studies to determine the activation energies for a variety of manganese and rhenium catalysts on the decomposition of potassium chlorate.

4. By analysis of residues to determine the state of the various catalysts after use in decomposition of potassium chlorate.

5. To construct an automatic recording balance designed to carry out the kinetic measurements.

6. To test the catalytic activity of some rhenium compounds on the decomposition of potassium chlorate, and to relate the catalytic activity of rhenium compounds to that of manganese compounds.

7. By use of oxygen^{18} isotope tracer techniques to check the proposal that catalytic activity of manganese dioxide on the decomposition of potassium chlorate involves a cyclic oxidation and reduction of the manganese.

RADIOCHLORINE^{36} AS A TRACER IN THE DECOMPOSITION OF $KClO_3$

Introduction

The thermal decomposition of potassium chlorate has been shown to be complex. Oxygen is evolved and, depending upon the conditions, various proportions of perchlorate are formed. At least two sets of equations have been proposed to explain the reaction. Otto and Fry (19) proposed that potassium chlorate decomposes by two simultaneous reactions.

A. $2KClO_3 \longrightarrow 2KCl + 3O_2$ (I)

$4KClO_3 \longrightarrow 3KClO_4 + KCl$ (II)

In a more recent publication Glasner and Weidenfeld (22,23), on the basis of kinetic data, suggested that reactions I and II are not simultaneous. Rather, the proposed that two consecutive reactions occur whereby atomic oxygen adds to chloride.

B. $KClO_3 \longrightarrow KCl + 3O$

$KCl + 4O \rightleftharpoons KClO_4$

An experiment was initiated to determine, if possible, which type of decomposition is correct. If proposal B is correct, a mixture of chlorate and radioactive chloride should yield radioactive perchlorate on decomposition.

While this experiment was in progress, Vanden Bosch and Aten (25) published a note reporting results of a similar study. Because they experienced difficulty in recrystallizing potassium perchlorate formed in their reaction mixtures, they used sodium salts instead of potassium salts. They decomposed sodium chlorate in the presence of sodium chloride containing Cl^{34} and Cl^{38} and found negligible activity in the resulting perchlorate. Thus, they did not confirm the proposal of Glasner and Weidenfeld (23).

In this experiment potassium chlorate and potassium chloride were used. $Chlorine^{36}$ was the radioactive tracer. Materials for this and all other experiments throughout the course of this investigation are included under the listing of materials for kinetic studies.

Preliminary Experiments

Preliminary experiments revealed that when a mixture of 0.2000 g. of $KClO_3$ and 0.0250 g. of KCl is heated in a pyrex tube at 510° C. for 60 minutes, a good yield of perchlorate is obtained in the residue. This is in accord with data reported by Glasner and Weidenfeld (23). When analyzed by standard methods (33) the residue from a preliminary experiment was found to contain 0.0725 g. of KCl, 0.0280 g. of $KClO_3$, and 0.099 g. of $KClO_4$. Further preliminary experiments showed that it was possible to isolate the chloride from each of these compounds.

Preliminary experiments were also carried out to find a satisfactory method for enriching KCl with Cl^{36} from HCl^{36}. It was proposed to neutralize the HCl with a slight excess of K_2CO_3 in the presence of KCl, and to evaporate to dryness. This would add KCl containing all the activity originally in the HCl. Difficulty was experienced, however, which led to an interesting discovery.

One and three-tenths ml. of 0.118 N HCl was added to 0.025 g. K_2CO_3 in the presence of 0.03 g. KCl, and the residue was dried and mixed with 0.2000 g. $KClO_3$. This mixture was heated in a pyrex tube in the furnace at 510° C. for one hour (treatment exactly like the treatment of samples in above preliminary experiments). Analysis of the residue by standard methods showed that the residue contained 0.149 g. KCl and no chlorate. The experiment was repeated and again after one hour at 510° C. the chlorate had completely decomposed.

The only difference in these and the previous mixtures was the presence of a small amount of K_2CO_3. Potassium carbonate, therefore, accelerates the decomposition of potassium chlorate. This result is contrary to a previous finding of Fowler and Grant (8) who reported that the rate of oxygen evolution during decomposition of potassium chlorate is retarded when sodium carbonate is present. This problem was not further investigated.

Since this method of preparing KCl^{36} would destroy the experiment, an exchange method was tried. A rapid isotopic exchange occurs between HCl and KCl (34). Further preliminary experiments revealed the feasibility of this method of preparation of KCl^{36} and HCl^{36}.

Preparation of KCl^{36}

The Cl^{36} was obtained as 1.4 N HCl^{36} with a specific activity of 0.23 mc/g., or 5.1×10^8 disintegrations per second. One tenth milliliter of this HCl^{36} was added to 0.0300 g. of KCl in a small pyrex test tube. The tube was placed in a closed system and distilled until the KCl residue was dry. Excess HCl^{36} was recovered. Since a rapid isotopic exchange occurs between HCl and KCl, the resulting KCl contained considerable activity. A sample was counted and found to have a relative activity of 9,296 counts per minute per milligram of chlorine (Sample 1, Tables I and II).

Procedure

A mixture of 0.2000 g. of $KClO_3$ and 0.0182 g. of KCl^{36} was heated at 510° C. for 62 minutes in a pyrex test tube extending into a vertical electric furnace. The residue was dissolved and the chloride was precipitated with excess silver nitrate. The precipitate was filtered on a weighed filter paper, washed, dried, and weighed according to standard methods (35). This precipitate is Sample 2, Tables I and II.

Ordinary KCl was added to the filtrate and previous wash water. The chloride was precipitated and weighed (Sample 3, Tables I and II). This was done to remove last traces of $chloride^{36}$ from the solution. Still a second quantity of ordinary KCl was added to the filtrate, precipitated with silver nitrate, and weighed (Sample 4, Tables I and II).

The filtrate was then evaporated to approximately 60 ml. and tank SO_2 was bubbled into the solution to reduce the chlorate to chloride (33). The resulting chloride was precipitated with silver nitrate, filtered, washed, and weighed (Sample 5, Tables I and II).

Another final quantity of wash KCl was added to the filtrate, precipitated as AgCl, and weighed (Sample 6, Tables I and II). Finally, the filtrate, containing only

Table I

Details of Counting

Sample	Times Counted	Δt.	Shelf	c/m	BG
1	6	2 min.	3	3356.3	30.2
2	1		(calculated)		
3	2	30 min.	1	294.2	30.2
3	2	30 min.	3	84.3	24.7
4	2	30 min.	1	46.8	24.6
5	2	30 min.	1	36.2	30.2
6	2	30 min.	1	29.9	30.2
7	3	30 min.	1	42.5	30.2

Table II

Results

Sample	Wt. AgCl (mg.)	Source	Wt. Cl (Calculated)	Shelf Factor	c/m-BG (shelf 1)	Spc.Act. (c/m/mg.)
1	6.3	KCl^{36}	1.6	3.36	14,502	9,296
2	109.7	Chloride	27.1	1	155,000[1]	5,720[1]
3	104.5	Wash KCl	25.8	1	264	10.1
4	76.2	2nd wash	18.8	1	22	1.2
5	14.0	$KClO_3$	3.3	1	6	1.8
6	102.8	Wash KCl	25.4	1	-.3	-.0
7	48.2	$KClO_4$[2]	12.3	1	13	1.1

[1] Calculated value.

[2] Weighed as $KClO_4$.

perchlorate, was evaporated to about 1 ml. Two ml. of ice water was added and the $KClO_4$ was filtered on a weighed filter paper, washed twice with cold water, twice with cold ether, and was weighed (Sample 7, Tables I and II). All samples were dried at 110° C. for one hour before weighing.

The radioactivity of these samples was determined by a 2C32 counter tube in an S-20 tube housing. The scaler was a Model 161, S-295 capable of counting 10,000 counts per minute.

The counter housing contained four shelves at different distances from the counter tube. Sample 3 was counted on both shelf 1 and 3 to find the shelf factor. Thus, samples of activity greater than 10,000 c/m could be counted on shelf 3, and its activity on shelf 1 could be calculated by multiplying by the shelf factor.

Results

The results of this experiment are summarized in Tables I and II. Table I records the details of the counting of samples. The second column lists the number of times each sample was counted, and the third column shows the duration of each counting period (Δt). Column 4 refers to the shelf on which the samples were placed in the counter tube housing. Column 5 shows the average counts per minute for each sample, and Column 6, the background count for the empty housing.

Table II lists the weight of each AgCl sample and the source of the chloride. (Sample 7 was weighed directly as $KClO_4$.) The fourth column shows the calculated weight of Cl in each sample. Column 5 lists the shelf factor used to calculate the activity of the samples to activity on shelf 1. The sixth column shows the activity of the samples, and the last column lists the calculated specific activity in counts per minute per milligram of Cl.

Sample 1 showed a specific activity of 9,296 c/m per milligram of Cl due to the presence of Cl^{36}. Sample 2, containing the chloride from the reaction mixture, had so much activity that its count was calculated by difference to contain approximately 155,000 c/m, a specific activity of 5,720 c/m per milligram of Cl. Sample 3 contained a specific activity of 10.1 c/m, an activity that one could expect to remain from Sample 2 due to the slight solubility of AgCl. The remaining samples contained relatively small specific activities.

Discussion of Results and Conclusions

The total activity in counts per minute in the original reaction mixture was obtained by multiplying the specific activity of the KCl^{36} (Sample 1) times the weight of KCl^{36}

in the chlorate-chloride mixture. This gave an activity of 9,296 c/m X 18.2 mg. = 169,164 c/m milligram.

In the original mixture (0.0182 g. KCl + 0.200 g. $KClO_3$) 13.01% of the total Cl was radioactive. The data also show that 18.5% of the total Cl ended up as perchlorate. If perchlorate were formed by the addition of oxygen to chloride, 13.01% X 18.5% = 2.41% of the activity could have been in the perchlorate. 2.41% of 169,164 = 4,177 c/m, corresponding to a specific activity of 339 c/m per milligram.

The data (Table II, Column 7) shows a specific activity of no more than 1.1 c/m per milligram. Thus, these results refute the proposal that potassium perchlorate is formed by the addition of oxygen to chloride during the decomposition of chlorate.

The data also show (Table II, Column 7) that the chlorate contained a specific activity of only 1.8 c/m per milligram of Cl. The relatively small activity in both the chlorate and perchlorate leads to the further conclusion that chloride does not appreciably undergo isotopic exchange with chlorate or perchlorate at 510° C.

PREPARATION AND SOME PROPERTIES OF MANGANESE (II) CHLORATE

Preliminary Experiments

Manganese chlorate, prepared in solution, was reported as early as 1843 (31). The compound itself has not previously been described. Brown and Woods (36) published its preparation and properties.

In preliminary experiments manganese chlorate solutions were prepared by reacting equivalent quantities of $MnSO_4$ and $Ba(ClO_3)_2$ and removing the insoluble $BaSO_4$. Preliminary experiments on these solutions revealed the following results:

1. A dilute solution, on standing in a test tube two days, decomposed, forming a black precipitate and yielding an odor resembling chlorine.

2. Upon concentrating a solution rapidly on a steam plate decomposition increased in vigor to explosiveness, yielding a yellow-green gas and a black residue.

3. When 10 ml. of solution was evaporated in a vacuum desiccator at room temperature, the solution was concentrated until a definite pink was observed before the solution darkened due to decomposition. Further concentration at room temperature resulted

in rapid decomposition. A yellow-green gas filled the desiccator and on standing, a colorless, oily film condensed on the sides of the desiccator. This oily film yielded chlorine when treated with concentrated H_2SO_4. It exploded when disturbed.

4. Another solution was concentrated and it decomposed. The yellow-green gas was condensed in an acetone-dry ice trap to form an orange-red solid. On warming this solid to room temperature, again a colorless, oily liquid film deposited on the sides of the vessel. A green gas was formed.

These preliminary experiments confirmed that $Mn(ClO_3)_2$ is unstable at room temperature. They also revealed that ClO_2 is a product of the decomposition. ClO_2 is a yellow-green gas which freezes to an orange-red solid. It disproportionates to form Cl_2 and Cl_2O_7. Cl_2O_7 is an explosive, oily liquid at room temperature, which yields chlorine upon treatment with concentrated H_2SO_4 (37).

Preparation and Analysis of Compound

Equivalent quantities of $MnSO_4$ and $Ba(ClO_3)_2$ were weighed out and mixed. Water was added to the mixture with stirring. Centrifugation removed the $BaSO_4$ and the resulting solution of $Mn(ClO_3)_2$ was used in the preparation. The

$Mn(ClO_3)_2$ was not washed from the $BaSO_4$ since it was desirable to keep the solution as concentrated as possible, so that excess water need not later be removed. Instead, for subsequent experiments manganese in the $BaSO_4$ was determined and subtracted from the original weight of manganese, in order to know the total weight of $Mn(ClO_3)_2$ in the solution.

Figure 1 is a diagram of the apparatus used to remove water from the $Mn(ClO_3)_2$ solution at low temperature. Three ml. of solution was placed in tube C inside one arm of U-tube. This arm extended into a freezing mixture of ice and brine in vacuum bottle A. The other arm of the U-tube extended into a colder mixture, acetone-dry ice, in vacuum bottle B. Air was removed from the U-tube by evacuation through stop-cock D. Ice from the solution in tube C condensed in the colder arm of the U-tube. In three days the 3 ml. of solution had evaporated to approximately 1 ml. The solution at this point was liquid at 0° C., but was frozen at -80° C.

Then acetone-dry ice was placed in vacuum bottle A and liquid nitrogen was placed in B. After four more days the solution had evaporated to approximately 0.2 ml. Further evaporation would not take place.

Figure 2 is a diagram of the apparatus used in

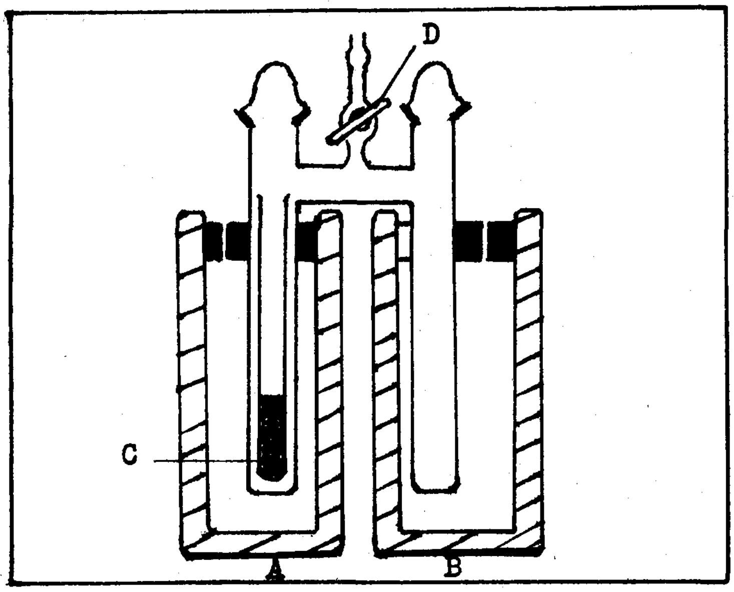

Figure 1. Apparatus for Removing Water from Solution at Low Temperature

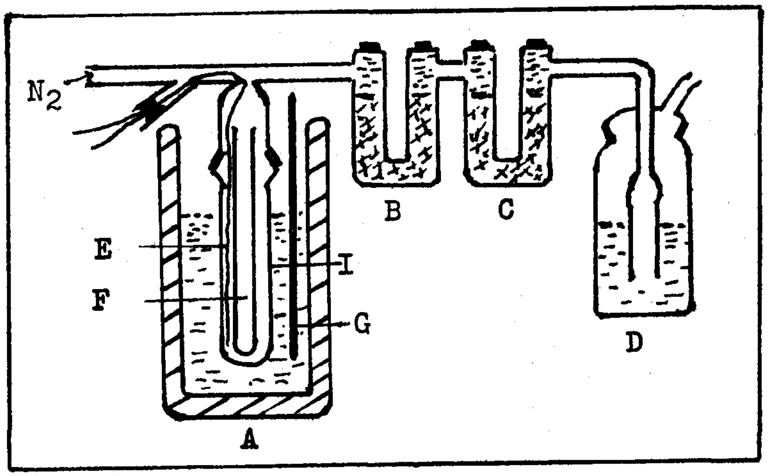

Figure 2. Apparatus Used in Analysis of Product

analyzing the manganese chlorate residue. The product in tube F was transferred to tube I extending into a vacuum bottle A containing acetone at -80° C. The acetone was allowed to warm slowly (about 1° per four minutes) until decomposition of the product was complete. The temperature was followed by a thermocouple E and a thermometer G.

Dry nitrogen was used to sweep volatile decomposition products through the apparatus. The U-tube B contained anhydrone. In it water vapor was collected and weighed. U-tube C was a drying tube which prevented back diffusion of water vapour. After the decomposition was complete, tube I was warmed with a burner to make sure all of the water was driven into U-tube B.

Bottle D contained an excess of standard KOH solution to collect and determine the ClO_2. The excess KOH was determined by titration with standard HCl. One mole of ClO_2 reacts with one equivalent of KOH (37).

The black residue in tube F was weighed. Manganese was determined in this residue by the bismuthate method (38).

Results and Discussion

The $Mn(ClO_3)_2$ product was a pink solid at -80° C. Observation of the product as it slowly warmed showed that it melted to a viscous, pink liquid at -18° to -15° C. At

-13° C. very slow decomposition began. At -5° C. decomposition was rather slow, but at 6° C. decomposition increased in vigor. At this point tube I (Figure 2) was warmed slightly. Increased decomposition resulted which could be slowed somewhat by a cold bath at 10° C. On rewarming to approximately 20° C. the residue exploded with a sharp report.

Table III shows the results of two experiments from which the formula of the manganese chlorate compound was calculated. In the third column for comparison is theoretical data for 1.0000 g. of $Mn(ClO_3)_2$ in manganese (II) chlorate hexahydrate.

The data indicate that manganese chlorate retains water of hydration that cannot be removed by this method. Results of the two experiments do not agree precisely on the number of water molecules of hydration. Experimental errors were large enough, however, to cause this much uncertainty. An average of the two sets of data lead to the conclusion that manganese (II) chlorate hexahydrate, $Mn(ClO_3)_2 \cdot 6H_2O$, is the product. This is reasonable since it is known that other manganese (II) salts form hexahydrates.

$Mn(ClO_3)_2 \cdot 6H_2O$ is a pink solid that melts to a viscous liquid at -15° to -18° C. and decomposes explosively at

Table III

Results of Experiments

	Expt. 1	Expt. 2	Theoretical for $Mn(ClO_3)_2 \cdot 6H_2O$
Wt. of $Mn(ClO_3)_2$ in tube	0.2008 g.	0.1690 g.	1.0000 g.
Wt. of residue after decomposition	0.0725	0.0777	0.3917
Wt. of Mn in residue	0.0471	0.0549	0.2475
Wt. of Cl_2 (from ClO_2)	0.0468	0.0500	0.3196
H_2O from decomposition	0.1027	0.0771	0.5143
Ratio of H_2O to one $Mn(ClO_3)_2$ (Calculated):			
a. From total $Mn(ClO_3)_2$	6.3	5.3	6.0
b. From manganese	6.7	5.3	6.0
c. From chlorine	6.6	5.6	6.0
Ratio of oxygen atoms to one manganese atom in residue oxide	1.7	2.9	2.0

6° to 10° C. Its decomposition corresponds to the following equation:

$$Mn(ClO_3)_2 \cdot 6H_2O \longrightarrow MnO_2 + 2ClO_2 + 6H_2O$$

When potassium chlorate is catalytically decomposed with manganese catalysts at high temperatures, oxygen, not chlorine, is evolved. When manganese chlorate decomposes at low temperatures, chlorine dioxide is given off.

Chlorine dioxide would decompose to give oxygen and chlorine at higher temperatures. Therefore, the absence of chlorine during catalytic decomposition of potassium chlorate, using manganese catalysts, leads to the conclusion that manganese chlorate is not involved in the catalysis, or that manganese chlorate does not decompose at [illegible]0° C. by the same mechanism as it does at 300°-400° C.

KINETIC STUDIES

Apparatus

Design and construction of an automatic recording balance

Introduction. Previous workers, in studying the decomposition of potassium chlorate, usually measured the rate of oxygen evolution volumetrically. Volumes of oxygen at various time intervals were measured, and the rate curve was obtained from a succession of points. For slow reactions manual volumetric measurements are tedious and have not been carried out over time intervals of more than a few hours.

Rates can also be measured by a series of weighings of the residue at various time intervals during oxygen evolution. However, this would require alternate cooling and heating the reaction mixtures between weighings. It became desirable to have an instrument that could accurately and automatically plot changes in weight due to oxygen evolution as a function of time, at constant temperature, over extended periods.

Gregg and Wintle (39) devised a glass automatic electrical sorption balance. Gregg (40) later described a recording system for this type balance. Eyrand (41) reported a glass sorption balance of a somewhat different type. Duval (42) described a thermal balance that automatically records changes in weight on film. Brown, Loomis, Peabody, and Woods (43) designed and constructed the balance here described. It was used in the kinetic studies reported in this thesis.

This instrument consists of three basic units: the balance (Fig. 3-b), the electronic control unit (Fig. 3-c), and the recorder (Fig. 3-f). The materials for the construction of these units are standard and easily available with the exception of the recorder. The design is such, however, that many types of recorders could be used. Each basic unit will be described below.

Balance. The balance (Fig. 3-b) is a slightly modified ordinary analytical balance from which the pan supports were removed and ¼ inch holes were bored through the bottom of the pans and balance case. Pyrex glass rods are suspended from hooks on the balance arms through these holes. A pyrex tube (6" x .5") reaction vessel hangs from the left rod into the constant temperature furnace mounted below the balance. On the right rod is suspended a 1 x 6 cm. Alnico magnet sealed in a glass tube which hangs within the core of the coils attached to the electronic control unit. The details of these hand-wound coils are shown in Table IV.

A small mirror (1 cm. x 1 cm.) is mounted exactly in the center of the balance beam. The mirror is masked with

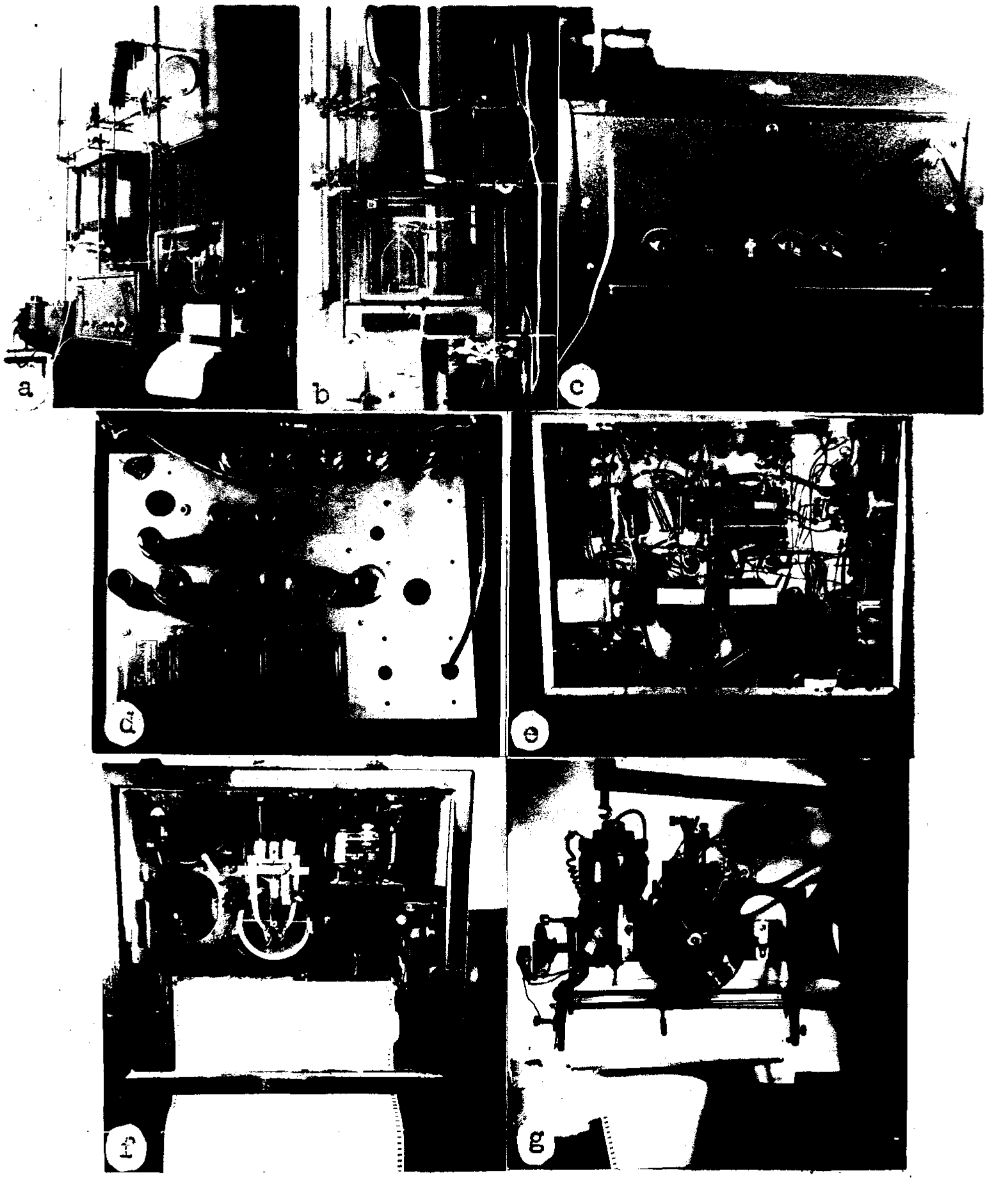

Figure 3. Automatic Recording Balance

a. Balance in operation.
b. Balance.
c. Electronic control unit.
d. Electronic chassis, upper view.
e. Electronic chassis, bottom view.
f. Recorder.
g. Rear view of recorder, showing drum potentiometer.

Table IV

Details of Control Coil Windings

Coil	Length	Core	Wire Used	Diameter over Winding	Resistance
Control Coil	5 cm.	4 cm.	27 B.&S. enameled Cu.	5.5 cm.	Approx. 115 ohms
Damping Coil (Double Winding)	5 cm.	4 cm.	32 B.&S. enameled Cu.	6.5 cm.	Approx. 110 ohms (each winding)

black paper to leave in its center a circle 2 mm. in diameter. A light beam is focused from an approximately 45° angle onto the mirror from a light source mounted above the balance case (Fig. 3-b). The light source is a 6-volt No. 82 bulb mounted in a housing. A lens in front of the bulb focuses the filament image onto the mirror. This image is then reflected through a reading glass lens onto a dual photocell mounted in a housing above the balance (Fig. 3-a & b).

<u>Electronic control unit.</u> The electronic control unit (Fig. 4) was designed to provide the maximum reliability and sensitivity consistent with low cost and ease of construction. Only parts which are readily available from standard radio supply houses are incorporated in the circuit. Where possible, conventional designs for power

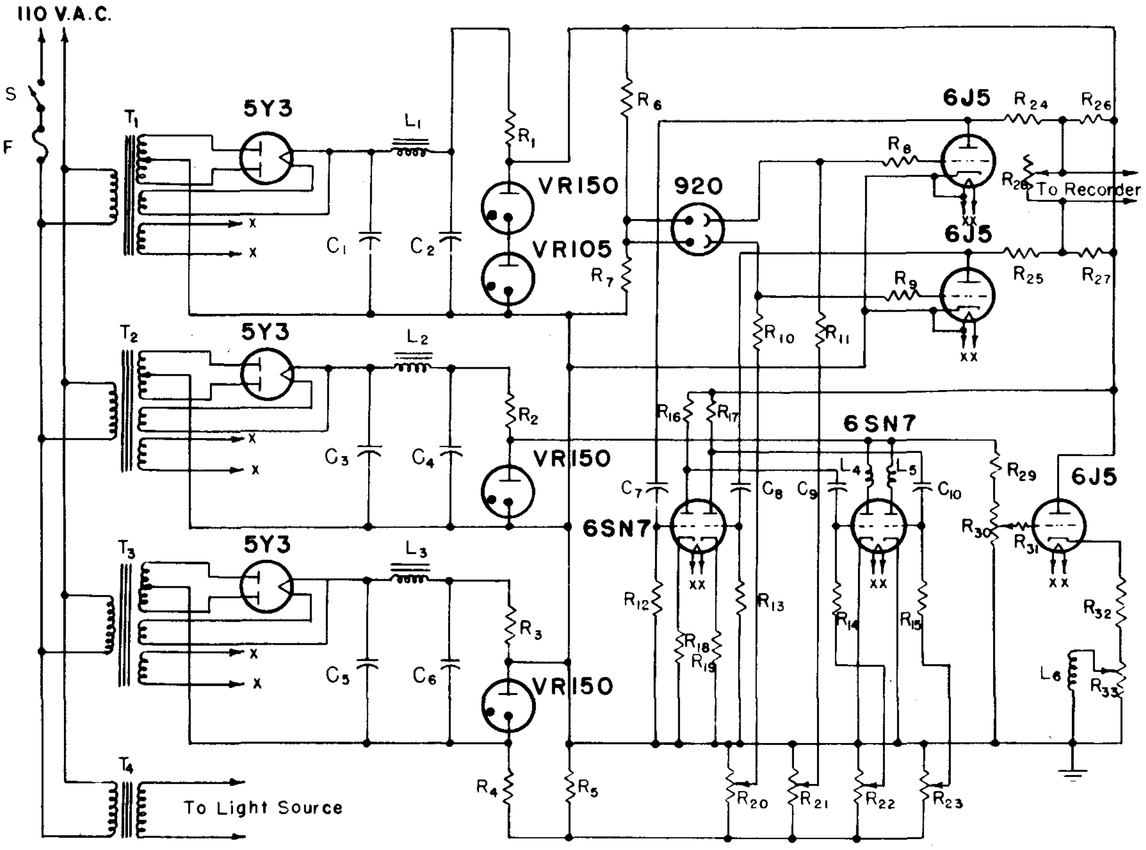

Fig. 4. Circuit Diagram

supplies, amplifiers, etc., are used. Since no high frequency circuits are employed, the construction of this instrument requires no great skill, and the chassis layout is not critical. Ability to use a soldering iron and hand tools is about all that is required of the builder of this instrument.

For the most part, strict adherence to the specifications regarding electrical size of components (Table V) is not necessary. A person with some knowledge of electronic circuits can easily modify the design to facilitate utilization of electronic parts that the builder may already have on hand. Modifications of the circuit will be necessary in the event that it is desired to use a recorder not of the old mechanical type described in this paper.

All of the d.c. power supplies are regulated by means of glow discharge, gas-filled voltage regulator tubes. This is the simplest type of regulation and is sufficient only if the input voltage is fairly constant. The writers found it expedient to obtain the 110 V. A.C. input from 220 volt line by means of a step-down transformer. This 220 volt source was not subject to the extreme voltage variations found in the 110 volt line. Provided the frequency of the source does not vary, a constant voltage transformer of the magnetic saturation type may be employed

Table V

Electronic Parts List*

C_1, C_2, C_3, C_4, C_5, C_6--10 mfd. electrolytic, 450 V.
C_7, C_8--5 mfd. paper, 400 V.
C_9, C_{10}--0.1 mfd. paper, 400 V.

L_1, L_2, L_3--Filter choke, 16 hys., 50 m.a.
L_4, L_5--Damping coils.
L_6--Main control coil.

F--Fuse, 5 amp.

R_1--1500 ohms, 5 watt.
R_2, R_3--10,000 ohms, 10 watt.
R_4--50,000 ohms, 1 watt.
R_5--5,000 ohms, 1 watt.
R_6--160,000 ohms, ½ watt.

R_7--220,000 ohms, ½ watt.
R_8, R_9--4 megohns, ½ watt.
R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}--1 megohn, ½ watt.
R_{16}, R_{17}--25,000 ohm, 1 watt.
R_{18}, R_{19}--1500 ohm, 1 watt.

R_{20}, R_{21}, R_{22}, R_{23}--Potentiometer, linear taper, 500,000 ohms.
R_{24}, R_{25}--2500 ohm, 1 watt.
R_{26}, R_{27}--50 ohm, 1 watt.
R_{28}--100,000 ohms, ½ ohm, 1 watt.
R_{29}--Potentiometer, linear taper, 100 ohms.

R_{30}--Drum potentiometer, linear taper, linearity tolerance--0.5%, 10,000 ohms.
R_{31}--250,000 ohms, 1 watt.
R_{32}--10,000 ohms, 1 watt.
R_{33}--Potentiometer, linear taper, wire-wound, 500 ohms.

S--Swith, SPST., toggle.

T_1, T_3--Power transformer, 235-0-235 volts rms., 40 ma.
T_2--Power transformer, 300-0-300 volts rms., 70 ma.
T_4--Filament transformer, 6.3 volts rms., 6 amp.

*Symbols refer to Circuit Diagram (Fig. 4).

for preliminary stabilization of the a.c. input. The rectifier and filtering circuits used are of conventional design and have a nominal current carrying capacity of about 40 ma. The power supplies are all contained in the main chassis assembly.

The photocell and the first amplifier stages are contained in a separate housing made from a 4" x 5" x 3" utility cabinet. This cabinet, complete with built-in chassis, may be obtained from almost any radio supply house.

The parts mounted in this cabinet are the 920 phototube, the two 6J5 amplifier tubes, resistors R_6, R_7, R_8, R_9, R_{10}, and R_{11}, and the potentiometers R_{20} and R_{21}.

An external mounting plate and hood for the phototube was constructed from light-weight sheet metal and fastened to the cabinet with self-tapping screws. The cabinet was fitted with a brass rod for mounting in an ordinary ring-stand clamp. This chassis is connected with the main chassis assembly by means of a seven-conductor shielded cable with an eight-contact multiwire cable connector mounted in the main chassis assembly.

The 920 phototube employed is a twin-unit gas-filled type with maximum sensitivity in the range of 800 to 1000 mu. This is the best spectral sensitivity for use when an ordinary incandescent bulb is the light source. The 6J5 triodes which constitute the first stage of amplification of the photocell current are mounted close to the phototube to provide short leads for the extremely small currents from the phototube. The apparent sensitivity of each half of the photocell can be varied independently by means of the potentiometers (R_{20} and R_{21}, Fig. 4) which control the grid bias voltage of the amplifier tubes.

The output of the photocell amplifiers is applied to the recorder terminals through a bridge circuit (R_{24-27}) and also to the damping circuit described below. A 100 ohm variable resistor (R_{28}) shunted across the recorder terminals provides for adjustment of the recorder response.

Attached to the shaft of the recorder pen mechanism is a 10,000 ohm precision linear potentiometer R_{30}. This potentiometer supplies to the cathode follower amplifier tube a grid voltage which varies with the motion of the recorder pen. The plate (and cathode) current of this tube is in direct and linear proportion to the grid voltage applied and hence is directly dependent on the position of the recorder pen. A portion of this current is fed to the main control coil L_6 thus supplying a magnetic field which is controlled in a linear manner by the recorder pen mechanism. This magnetic field surrounding the Alnico magnet suspended from the balance beam controls the position of the beam. The fraction of the total cathode follower current that is applied to the control coil may be varied by the 500 ohm potentiometer (R_{33}) in the cathode supply. This provides a means for adjusting the range (number of chart paper divisions per milligram) of the balance.

A time lag between a change in the magnetic field of the control coil and the response of the balance beam always exists due to inertia of the beam. This results in a continual over-correction whenever there is a change in weight of the sample. If no provision were made for this over-correction, the balance would then remain in continual oscillation. The operation of the damping circuit incorporated in this instrument to eliminate this difficulty may be described as follows:

Consider the light beam from the mirror on the balance beam to be sweeping onto the top cathode of the 920 phototube in Fig. 4. The rate at which this occurs depends upon the natural period of oscillation of the balance. As the illumination increases, the current through that half of the phototube increases and causes the following series of events:

1. The voltage drop across R_{11} resulting from the increased current through R_{11} makes the grid of the top 6J5 more positive.

2. Raising the grid potential increases the plate current and lowers the potential at the plate due to a larger IR drop in the resistors R_{24} and R_{26}.

3. This reduces the current through the coupling condenser C_7 and resistor R_{12} lowering the grid potential of that half of the first 6SN7 amplifier tube. No differentiation of the voltage across C_7 and R_{12} occurs because the time constant $R_{12} \times C_7$ (20 sec.) is long compared with the period of the balance.

4. The plate current in that half of the second 6SN7 decreases causing a reduction in the IR drop across R_{16}. The potential at the plate and hence at the top of the condenser C_9 increases.

5. C_9 and R_{14} constitute a simple differentiating circuit since the time constant $C_9 \times R_{14}$ is small (0.1 sec.) compared with the time required for the light beam to swing completely onto the phototube (i.e., the period of the balance). Thus as the voltage applied to C_9 increases, an instantaneous voltage is produced across R_{14} which is proportional to the differential with respect to time of the voltage applied across C_9 and R_{14}.

6. This voltage across R_{14} makes the grid potential of that half of the 6SN7 more positive causing a current to flow in the damping coil L_4. The overall result is that the current flowing in L_4 is proportional to the rate at which the light beam is moving onto the phototube which is also the rate at which the balance

beam is swinging. Since this tube is biased below cut-off by means of the damping control potentiometer, R_{22}, no current flows in the damping coil unless the illumination of the phototube is increasing. An exactly parallel operation occurs when the beam swings in the opposite direction. The current which flows in the damping coils in either case is such that the magnetic field which is set up tends to oppose the motion of the magnet, restoring the beam to the equilibrium position.

Recorder. The recorder(Fig. 3-f) is an old revamped Leeds and Northrop temperature recorder. A constant speed motor, the speed of which can be controlled by an adjustable governor, turns a roller for the chart paper. A cammed drive shaft operates a drum pen mechanism. The pen mechanism is controlled by a galvanometer which is deflected to and fro in response to swings of the balance beam.

Attached directly to the shaft of the pen mechanism is a 10,000 ohm linear drum potentiometer (Fig. 3-g) which turns with the pen mechanism a number of degrees proportional to the deflection of the galvanometer needle. This potentiometer varies the amount of current flowing in the control coils in such a sense as to tend to restore the balance to a null position.

Operation of instrument. The instrument operates on 110 volts A.C. Several controls are used in its operation. Two photocell potentiometers are mounted on the photocell housing (Fig. 3-b). These vary the sensitivity of the photocells and are set to zero the galvanometer needle of the recorder when the balance is at its zero point. Other controls are mounted on the panel of the electronic control unit. These will be described from left to right as shown in Figure 3-c. First is a sensitivity control which is used to determine the extent of deflection of the recorder galvanometer needle for a given deflection of the balance beam. Next is a fuse box, then the master switch for the electronic control unit and light source. The next two controls are used to adjust the amount of damping required. They operate in parallel, each controlling one damping circuit. At the right side of the panel is the range control which determines the number of lines on the chart paper that corresponds to a given change in weight.

After a warm up period the balance beam is locked and the recorder galvanometer needle is zeroed by the photocell potentiometers. The balance beam is unlocked and tares are added to one balance pan until the recorder drives the pen to the desired position on the chart paper. The damping controls are turned clockwise in parallel until sufficient damping is observed. Once the proper damping is found, very little further adjustment of these controls is needed. The range is found by setting the range control and observing the plot made when a given weight is added to one balance pan. Turning the range control in a clockwise direction decreases the range. The chart paper speed can be changed by a screw adjustment on the governor of the recorder motor.

Finally a weighed load is introduced into the reaction vessel and tared by an equal weight placed on the right pan of the balance. The instrument then automatically plots any changes in weight of the load as a function of time.

The range of this instrument is adjustable by the range control from 100 milligrams to 25 milligrams per chart-paper width. This range could be further increased by a small modification in the electronic circuit. Changes in weight are recorded with an accuracy of 0.5%. The instrument is reproducible to 0.1 milligrams. Over extended periods of time the uncertainty is ±0.2 milligrams. Although the electronic control unit contains voltage regulators, excessive fluctuations of line voltage can result in increased uncertainty. By using a 220 volt source, which is usually more constant, and a transformer for converting to 110 volts, this uncertainty can be decreased.

Constant temperature furnace

The furnace used in these experiments (Fig. 3-b) was made by wrapping a resistance wire heating coil around an insulated 1" x 12" iron tube. Another auxiliary control coil of resistance wire was wrapped around the insulated heating coil. The tube was then inserted through holes in the ends of a 5" x 10" tin can which was stuffed with powdered asbestos. The whole furnace was then covered by several layers of asbestos paper.

The heating coil was connected through a variac to a 110 volt source. A thermoregulator was mounted in the bottom of the iron tube. This thermoregulator, connected to a sensitive Fisher type relay, controlled current in the control coil which received current from a variac source in series with the relay. A control on the thermoregulator allowed adjustment to a desired temperature.

The temperature of the furnace was measured by a chromel-alumel thermocouple inserted into a hole in the side of the furnace, extending into a hole in the center of the iron tube. Potential difference was read in millivolts from a Leeds and Northrup potentiometer and calculated to temperature on the centigrade scale.

The whole furnace was encased in an asbestos-lined, wooden box mounted below the automatic recording balance. The pyrex glass rod from the left arm of the balance beam extended through a small hole in the top of the box. A hook on the end of the rod suspended the reaction tubes in the iron tube of the furnace.

This furnace would maintain a constant temperature within ±2° C. over extended periods of time.

Reaction tubes

The reaction tubes used for the kinetic studies were 11-12 mm. pyrex tubes, 15 cm. long. At opposite sides of the open ends were small glass projections. A nichrome wire bail with hooks was used for suspending these tubes by the glass projections to the pyrex glass rod from the balance beam. A small glass cap was fitted loosely in the top of the tube to catch any solids that might be mechanically carried from the reaction tube.

For studies using rhenium catalysts, similar but longer reaction tubes were used (11-12 mm. x 22 cm.).

Materials

Catalysts used

Following is a list of compounds used as catalysts for this study. The list includes the source of each compound, or the method of its preparation, and in most cases the results of a chemical analysis.

Manganese was determined in the manganese oxides by the bismuthate method (38). Rhenium oxides were analyzed by dissolving in superoxal, boiling off the excess H_2O_2, and titrating the resulting $HReO_4$ with standard KOH, as described by Feit and Donhart (44) and by Maun (45). The potassium perrhenate was analyzed by the method of Willard and Smith (46) in which ReO_4^- is precipitated with tetraphenyl arsonium chloride.

(1) Manganese metal, Mn: Baker and Adamson. (98.8% Mn by analysis)

(2) Manganous oxide, MnO: Prepared by heating 3 grams of Baker and Adamson reagent grade MnO_2 in an atmosphere of hydrogen at 550° C. for 8 hours. (74.1% Mn, corresponds to $MnO_{1.2}$)

(3) Mangano-manganic oxide, Mn_3O_4: Prepared according to Myers and Kanters (47) by heating Baker and Adamson reagent grade MnO_2 in a platinum

crucible in an electric furnace for 27 hours at approximately 1000° C. The product appeared reddish brown in color as described in the literature.

(66.1% Mn, corresponds to $MnO_{1.7}$)

(4) Manganese trioxide, Mn_2O_3: Prepared according to Myers and Kanters (47) by heating Baker and Adamson reagent grade MnO_2 in a porcelain crucible in an electric furnace for 20 hours at 700° C. The product appeared purple-brown in color.

(69.59% Mn, corresponds to $MnO_{1.55}$)

(5) Manganese dioxide, MnO_2: Baker and Adamson reagent grade.

(63.9% Mn, corresponds to $MnO_{2.1}$)

(6) Manganese dioxide, MnO_2: Specially prepared catalyst by Fisher Scientific Company (48).

(53.6% Mn, corresponds to $MnO_{2.7}$ or $MnO_2 \cdot H_2O$)

(7) Manganese dioxide, MnO_2: Specially prepared as follows: Approximately 6 grams of Baker and Adamson, reagent grade, $KMnO_4$ was dissolved in 200 ml. of water. 100 ml. of methyl alcohol was added, stirred, and allowed to stand 10 hours. A red-brown precipitate resulted. The precipitate was filtered on a sintered glass filter, washed three times with methyl alcohol,

and was dried at 110° C. for 24 hours. The oxide was red-brown in color. (55.9% Mn, corresponds to $MnO_{2.8}$ or $MnO_2 \cdot H_2O$)

(8) Potassium permanganate, $KMnO_4$: Baker and Adamson, reagent grade.

(9) Rhenium metal, Re: From City Chemical Corporation. (98.6% Re)

(10) Rhenium dioxide, ReO_2: Prepared by heating approximately 0.5 g. of ReO_3 in an evacuated tube at 450° C. for 16 hours (37). The ReO_3 disproportionated into ReO_2 and Re_2O_7. The Re_2O_7 sublimed to the cool end of the tube and left the ReO_2 behind. Cutting the tube in two separated the ReO_2 from the Re_2O_7. The ReO_2 was black as described in the literature. (72.7% Re, corresponds to 85.3% ReO_2)

(11) Rhenium trioxide, ReO_3: Prepared according to Maun (45) and according to Nechamkin, et al (49) by treating approximately 0.5 g. of Re_2O_7 with dioxane which had been freshly distilled over sodium to dry it. A gray-white precipitate formed, having a melting point of 90°-100° C. This corresponded to the melting point of the same compound, rhenium dioxanate, described by Nechamkin, et al (49). The gray-white precipitate

was dried at room temperature and then was placed in a furnace at 145° C. for one hour. A burnt sugar odor was observed. A red, crystalline material resulted.
(72.6% Re, corresponds to 91.3% ReO_3)

(12) Rhenium heptaoxide Re_2O_7: Prepared by oxidation of 0.5 g. of rhenium metal in an atmosphere of oxygen at 450° C. for 8 hours. A canary yellow material sublimed to the cool portion of the reaction tube.
(Not analyzed, but assumed to be pure since it was sublimed.)

(13) Potassium perrhenate, $KReO_4$: Prepared by reacting Re_2O_7 with water, titrating the resulting $HReO_4$ with KOH, and evaporating to dryness.
(87.5% $KReO_4$)

Reagents and chemicals

The following list of chemicals include those used throughout the course of this study and the other studies in this thesis. The list does not include chemicals used incidentally, such as indicators for titrations.

(1) Acetone, $(CH_3)_2CO$: Baker and Adamson, reagent grade.

(2) Barium Chlorate, $Ba(ClO_3)_2$: Baker and Adamson, reagent grade.

(3) Calcium Carbonate, $CaCO_3$: Baker and Adamson, reagent grade. Chloride $< 0.001\%$.

(4) Ceric Sulfate, $Ce(HSO_4)_2$: G. Frederick Smith Chemical Company, Columbus, Ohio. GFS reagent.

(5) Chlorine^{36} Enriched HCl: Ames Laboratory, A.E.C. 1.4 N HCl^{36}, Specific Activity, 0.23 mc/g.

(6) Dioxane, $(CH_2)_4O_2$: Merck and Co., Inc. Dried by distillation over sodium.

(7) Ferrous Ammonium Sulfate, $Fe(NH_4)_2(SO_4)_2$: Baker and Adamson, reagent grade.

(8) Hydrochloric Acid, HCl: Baker and Adamson, reagent grade. Concentrated.

(9) Hydrogen Gas, H_2: Balback Co., Omaha, Nebraska.

(10) Hydrogen Peroxide, Superoxal, H_2O_2: Merck and Co., Inc. 30% H_2O_2.

(11) Manganese Metal, Mn: Baker and Adamson, 95%

(12) Manganese Chloride, $MnCl_2$: Baker and Adamson, reagent grade.

(13) Manganese Dioxide, MnO_2: Baker and Adamson, reagent grade.

(14) Manganese Sulfate, $MnSO_4 \cdot H_2O$: Baker and Adamson, reagent grade.

(15) Methanol, CH_3OH: Merck and Co., Inc.

(16) Nitric Acid, HNO_3: Baker and Adamson, reagent grade. Concentrated.

(17) Oxygen Gas, O_2: Balback Co., Omaha, Nebraska.

(18) Oxygen^{18} Enriched H_2O: Ames Laboratory, A.E.C.

(19) Potassium Chlorate, $KClO_3$: Baker and Adamson, reagent grade.

(20) Potassium Chloride, KCl: Baker and Adamson, reagent grade.

(21) Potassium Perchlorate, $KClO_4$: Baker and Adamson, reagent grade.

(22) Potassium Permanganate, $KMnO_4$: Baker and Adamson, reagent grade.

(23) Rhenium Metal, Re: City Chemical Corp., New York.

(24) Silver Nitrate, $AgNO_3$: Baker and Adamson, reagent grade.

(25) Sodium Carbonate, $NaCO_3$: Baker and Adamson, reagent grade.

(26) Sodium Bismuthate, $NaBiO_3$: Baker and Adamson, reagent grade.

(27) Sulfur Dioxide Gas, SO_2: Sargent Co., Chicago.

(28) Sulfuric Acid, H_2SO_4: Baker and Adamson, reagent grade. Concentrated.

(29) Tetraphenylarsonium Chloride, $(C_6H_5)_4AsCl$: Hack Chemical Co., Ames, Iowa.

Procedure

Preparation of mixtures

For measurement of reaction rates reaction samples were used of such size that each contained exactly one gram of $KClO_3$. This sample size was chosen to make convenient the calculations of rate constants. Also, one gram samples were easy to prepare and weigh out. Further, the decomposition of a one gram sample of potassium chlorate could be accurately and easily plotted by the automatic recording balance.

In order that catalytic activities of the various catalysts could be compared, each reaction sample was made to contain the same mole percent of manganese or rhenium. A composition of 1.4 mole percent manganese or rhenium was chosen. This composition corresponds to 1% manganese dioxide by weight, a type of mixture previously used when manganese dioxide was studied as a catalyst in the decomposition of potassium chlorate.

Reaction mixtures of potassium chlorate with manganese catalysts were prepared in batches containing 98.6 mole percent potassium chlorate and enough catalyst to contain 1.4 mole percent manganese. The potassium chlorate was ground in an agate mortar to pass a 100 mesh screen and was dried at 110° C. The catalysts were ground in an agate mortar to pass a 200 mesh screen.

Then 10.000 grams of the potassium chlorate and enough catalyst to contain 0.00115 moles of manganese were mixed and ground together in an agate mortar. The mixture was placed in a ground glass stoppered weighing bottle and shaken thoroughly. Later samples large enough to contain 1.0000 grams of $KClO_3$ were weighed out of these prepared batches.

Samples were weighed in a specially designed 1.5" x 0.5" funnel-shaped pyrex glass weighing boat. This weighing boat was convenient for pouring a sample into the reaction tube on the balance. A camel hair brush served to brush all the sample into the reaction tube.

Since the supply for rhenium catalysts was limited, a somewhat different procedure was employed in the preparation of mixtures using rhenium catalysts. In this case an individual sample for each run was prepared. A 1.0000 gram sample of $KClO_3$ was weighed out. Then enough rhenium catalyst to contain 0.00115 moles of rhenium was weighed out and mixed with the potassium chlorate by grinding together in an agate mortar. These samples were used as they were prepared.

It is significant to note that as the Re, ReO_3, and Re_2O_7 were being ground with the $KClO_3$, a faint chlorine-like odor was observed. The ReO_3 and Re_2O_7 mixtures took up moisture while grinding and caused the powdered $KClO_3$ to pack somewhat.

Measurement of reaction rates and calculations

The rate of decomposition of potassium chlorate in each sample was measured at constant temperature by placing the sample in a reaction tube suspended in the constant temperature furnace by the pyrex glass rod hanging from the beam of the automatic recording balance. Before each run the furnace was adjusted to the proper temperature. The balance was adjusted with a weighed reaction tube and loose fitting cap in place in the furnace. The balance beam was tared to place the recorder pen at the left of the chart paper and then was locked.

The sample was weighed in the weighing boat on an analytical balance. Weights corresponding to the exact weight of the sample were then placed on the right pan of the recording balance. The cap was raised from the reaction tube, the sample was brushed into the tube, and the cap was replaced. The balance was then unlocked. Zero time was marked on the chart paper. The recorder then plotted the loss in weight, due to oxygen evolution, as a function of time.

For these experiments the range of the recorder was set at 50 milligrams per chart paper width. Whenever 50 milligrams of oxygen had evolved, it was only necessary to place a 50 milligram weight on the left pan of the balance.

The pen would cross the paper and record until another 50 milligrams of oxygen had evolved.

Runs that were intended to go to completion were recorded until no more than 1 milligram of oxygen was liberated per hour. In some cases, however, the recorder was allowed to run a considerable time after this rate had been reached. This was to observe changes later that might occur in the composition of the residue after evolution of oxygen practically ceased. The reaction tube was then removed from the furnace, cooled, and weighed. The difference in weight of the tube before and after the reaction served as a check on the total weight of oxygen liberated as shown on the chart paper. Agreement within 2% was usual.

Reaction rates for mixtures of each catalyst were measured in this manner at two or more temperatures. Samples from all mixtures were run at 340° C. and at 366° C. Several samples of mixtures were also run at other temperatures. The decomposition rate for pure potassium chlorate was necessarily measured at higher temperatures: 366° C., 455° C., 503° C., and 527° C. Lower temperatures were used for the Fisher MnO_2 mixture: 366° C., 340° C., 312° C., 284° C., and 231° C.

In order to obtain specific reaction rate constants for the reactions, it was necessary to know or assume the order of the reactions. Tests for first and for second order kinetics were made on runs for the decomposition of pure potassium chlorate, and on runs for the decomposition of potassium chlorate with B.&A. manganese dioxide catalyst.

First order kinetics require a straight line for a plot of t vs log $\frac{a}{a-x}$ according to the first order rate law

$$kt = 2.303 \log \frac{a}{a-x}$$

where k is the specific rate constant, t is the time, a is the original concentration of the reactant, and x is the moles of product formed at time t. Since k is dimensionless, the units for a and x are not important. In these calculations a was 392 milligrams, the total weight of oxygen in 1.000 g. $KClO_3$. x was the milligrams of oxygen evolved at any time t.

The various t's and x's were read directly from the chart paper records from the automatic recording balance. A calibrated T square and drawing board were used to facilitate measuring the reaction curves to obtain the various t's and x's.

Samples of first order plots of t vs log $\frac{a}{a-x}$ for the decomposition of pure $KClO_3$ and for $KClO_3$ with B.&A. catalyst are shown in Figure 5, curves 1 and 3. The curves in Figure 5 are not all drawn to the same scale but are included on one plot for comparing the linearity of the lines.

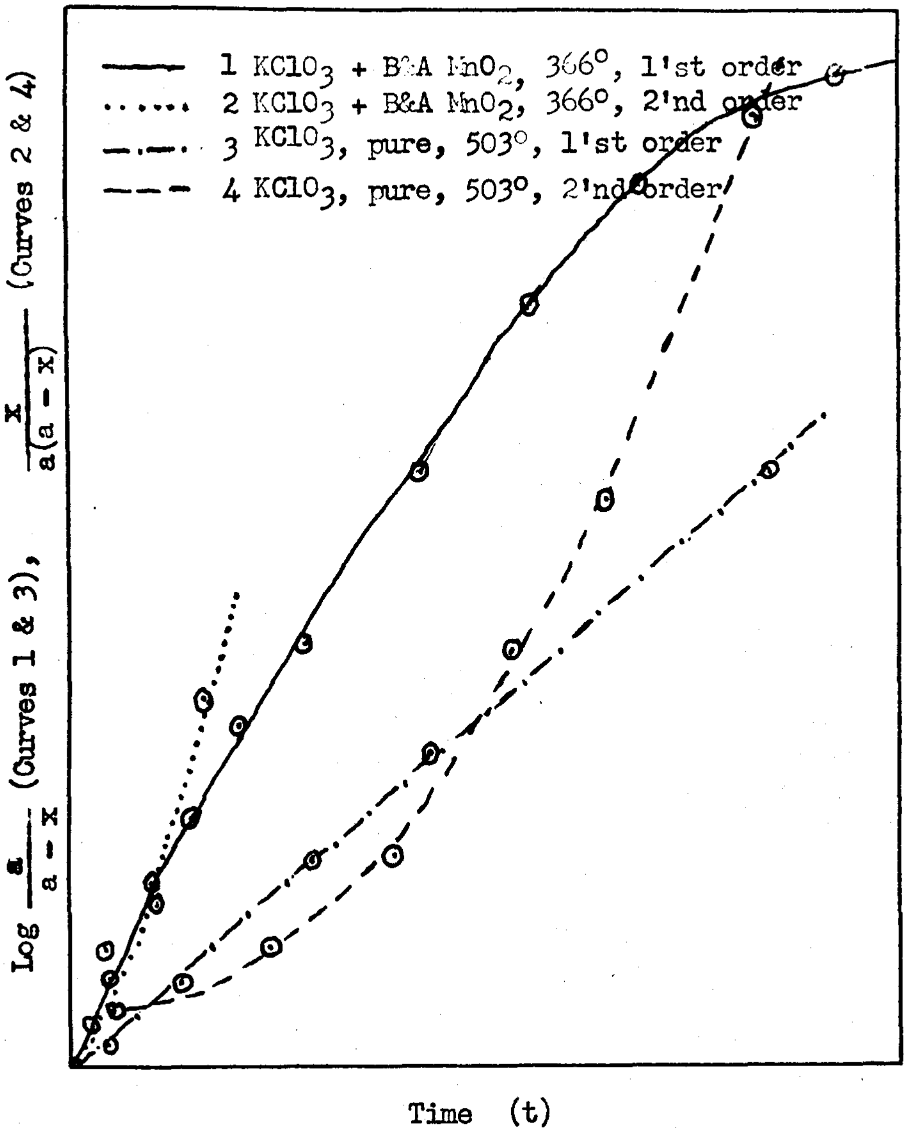

Figure 5. First and Second Order Rate Plots

Second order kinetics require a straight line for a plot of t vs $\frac{x}{a(a-x)}$ according to the second order rate law

$$kt = \frac{x}{a(a-x)}$$

where t is the time, a is the concentration of the reactant, and x is the concentration of product formed at time t. For this test a was $\frac{1.000}{KClO_3}$, the moles of $KClO_3$. The x was $\frac{2}{3} \times \frac{\text{wt. of oxygen}}{32}$, the moles of $KClO_3$ decomposed to yield a given weight of oxygen at time t, as measured on the chart paper. Samples of second order plots of t vs $\frac{x}{a(a-x)}$ are shown in Figure 5, curves 2 and 4.

Comparison of the two sets of curves (Figure 5) shows that for the first part of the reaction the first order rate law gives the best straight lines. Other such plots, using other rate laws, gave no better straight lines. Therefore, for purposes of obtaining apparent activation energies, specific reaction rate constants were obtained from first order plots of the various decomposition reactions. Activation energies for each reaction were calculated from the rate constants obtained at two temperatures, using the Arrhenius equation. In cases where runs for a single mixture were made at three or more temperatures, the activation energy was obtained from the slope of the plot of log k vs $\frac{1}{T}$. In these cases $E = 2.303 \times 1.987 \times$ slope.

Analysis of residues and calculations

The residues from most of the reactions were analyzed for chloride, chlorate, and perchlorate by standard methods (33). Samples containing manganese were analyzed for permanganate in the soluble portion and for manganese in the insoluble portion. Samples containing rhenium, with few exceptions, contained no insoluble portions. In the absence of a method for precipitating or determining perrhenate in the presence of chlorate or perchlorate, rhenium was not determined. However, absorption spectra in the ultraviolet were taken of these solutions to prove the presence of perrhenate in each case.

The first several samples were treated by a method which was slightly modified for later samples to increase the accuracy of the analyses. The first method will be described in detail and later modifications will be pointed out.

The residue of a sample was scraped from the reaction tube and ground in an agate mortar. A weighed sample of the residue was dissolved and diluted to a measured volume. Chloride in a 10 ml. aliquot was then titrated with standard silver nitrate by the Fajan (50) method. Into another 10 ml. aliquot SO_2 gas was bubbled for at least two minutes. This reduced any chlorate present to chloride without reducing perchlorate (33). The solution was then boiled to remove excess SO_2. On cooling, excess chloride-free calcium carbonate was added, and the chloride was titrated. Still another 10 ml. aliquot was evaporated to dryness and fused with excess sodium carbonate in a platinum crucible. The fusion decomposes both chlorate and perchlorate (51). The fusion product was then dissolved in water with dilute nitric acid, the excess nitric acid was neutralized with excess chloride-free calcium carbonate. Total chloride was then titrated. From data obtained chloride, chlorate, and perchlorate were calculated. The fusion was omitted in some instances in which cases perchlorate was obtained by difference.

For samples in which manganese catalysts were used, another weighed portion of the residue was treated with water and filtered in weighed, sintered glass filtering crucibles. The residue was washed with water and the washing added to the filtrate.

Permanganate in a pink filtrate was determined colorimetrically with a Beckman D. U. spectrophotometer by measuring percentage transmittancy of the solution at 520 $m\mu$. Permanganate in parts per million was determined by using a standard permanganate reference curve. Parts per million of permanganate was calculated to percentage of total manganese. Complete absorption spectra in the visible range were measured in a few of the solutions to confirm the assumption that the color was due to permanganate.

The insoluble portion of the residue in the filtering crucible was dried at 110° C. and was analyzed for manganese by the bismuthate method (38). The insoluble residue was dissolved with the aid of a few drops of concentrated HCl. A drop or two of 30% H_2O_2 was often added to hasten solution. Two to three ml. of concentrated H_2SO_4 were then added, and the solution was evaporated on a hot plate to remove excess HCl and H_2O_2. On cooling the solution was diluted to 100 ml. with H_2O. Three to five ml. of concentrated HNO_3 were added, and one to two grams of sodium bismuthate were stirred into the solution. Excess bismuthate was filtered off through a sintered glass filter, and the resulting permanganate was titrated with excess standard ferrous ammonium sulfate and back titrated with standard cerric sulfate.

In the later modification of this procedure the total residue was extracted with water and filtered, and the total residue was treated for manganese. The total filtrate was diluted in a volumetric flask and again 10 ml. aliquots were used to determine chloride, chlorate, and perchlorate. Permanganate was determined in any sample that gave a pink solution.

From the titration data the weight of manganese in the residue was calculated. From the weight of manganese and the weight of the residual oxide, the ratio of manganese atoms to oxygen atoms was calculated.

Following is a sample of the data and calculations obtained from the analysis of a residue from a reaction using a manganese catalyst:

Data: Mixture C, Run 23 (1.000 g. $KClO_3$ + 0.0091 g. Mn_2O_3).

Temperature of run	340° C.
Total wt. of oxygen evolved	0.025 g.
Wt. of residue	0.9833 g.
Volume of solution of soluble part of residue	50 ml.
Volume of 0.1001 N $AgNO_3$ to titrate 10 ml. aliquot	1.30 ml.
Volume to titrate 10 ml. aliquot after SO_2 treatment	14.89 ml.
Volume to titrate 10 ml. aliquot for total Cl	14.52 ml.
Percentage transmittancy for permanganate	95.2%
Parts per million of permanganate	1.5 p.p.m.
Wt. of insoluble part of residue	0.0072 g.
Volume of 0.1232 N $Fe(NH_4)_2(SO_4)_2$	4.00 ml.
Volume of 0.1024 N $Ce(SO_4)_2$	0.40 ml.

Calculations:

$$\text{Wt. of KCl} = 1.30 \times 0.1001 \times \frac{\text{KCl}}{1000} \times \frac{50}{10} = 0.0483 \text{ g.}$$

Wt. of $KClO_3$ = $\left[(14.89 \times 0.1001)-(1.30 \times 0.1001)\right] \times \frac{KClO_3}{1000} \times \frac{50}{10} = 0.834$ g.

Wt. of $KClO_4$ . . . . 0.0 g.

Wt. of $KClO_4$, by difference $= \frac{KClO_4}{KCl} \times \left[\frac{1.000 \times Cl}{KClO_3} - \left(\frac{0.0483}{KCl} - \frac{0.843 \times Cl}{KClO_3}\right)\right] = 0.0583$

Wt. of $KMnO_4 = \frac{1.5 \times 100}{10^6} = 1.5 \times 10^{-4}$ g.

Percentage of total Mn in $MnO_4 = \frac{1.5 \times 10^{-4}}{.0091} \times \frac{Mn}{KMnO_4} \times \frac{Mn_2O_3}{2Mn} = 0.8\%$

Wt. of Mn in insoluble part of residue $= \left[(4.00 \times 0.1232) - (0.40 \times 0.1024)\right] \times \frac{Mn}{5000} = 0.0049$ g.

Wt. of O = (0.0072 - 0.0049) = 0.0023 g.

Ratio of Mn to O $= \frac{0.0049}{54.93}$ to $\frac{0.0023}{16} = MnO_{1.6}$.

Following is a sample of the data and calculations obtained from the analysis of a residue from a reaction using a rhenium catalyst:

Data: Run 29 (1.000 g. $KClO_3$ + 0.0267 g. ReO_3).

Temperature of run	340° C.
Total wt. of oxygen evolved.	0.118 g.
Wt. of residue	0.9094 g.
Volume of solution of soluble part of residue.	50 ml.
Wt. of insoluble part of residue	0.00 g.
Volume of 0.1001 N $AgNO_3$ to titrate 10 ml. aliquot.	4.86 ml.

Data, continued:

Volume to titrate 10 ml. aliquot after SO_2 treatment . . . . 15.52 ml.

Volume to titrate 10 ml. aliquot for total Cl. . . . . 15.53 ml.

(Ultraviolet absorption spectrum was run on solution to ascertain presence of ReO_4^-.)

Calculations:

$$\text{Wt. of KCl} = 4.86 \times 0.1001 \times \frac{KCl}{1000} \times \frac{50}{10} = 0.1795 \text{ g.}$$

$$\text{Wt. of } KClO_3 = \left[(15.52 \times 0.1001) - 4.86 \times 0.1001)\right] \times \frac{KClO_3}{1000} \times \frac{50}{10} = 0.653 \text{ g.}$$

$$\text{Wt. of } KClO_4 = \left[(15.53 \times 0.1001) - (15.52 \times 0.1001)\right] \times \frac{KClO_4}{1000} \times \frac{50}{10} = 0.007 \text{ g.}$$

$$\text{Wt. of } KClO_4\text{, by difference} = \frac{KClO_4}{KCl} \times \left[\frac{1.000 \times Cl}{KClO_3} - \left(\frac{0.653 \times Cl}{KClO_3}\right)\right] = 0.0567 \text{ g.}$$

$$\text{Wt. of oxygen, calculated from wt. of KCl} = 0.1795 \times \frac{3O_2}{2KCl} = 0.116 \text{ g.}$$

Results and Discussion

Decomposition of pure $KClO_3$

Figure 6 shows the rate of decomposition of pure $KClO_3$ at various temperatures. Milligrams of oxygen from the recorder chart paper have been converted to percentage of oxygen evolved. The two broken curves are from data of Glasner and Weidenfeld (22) for comparison. Although the

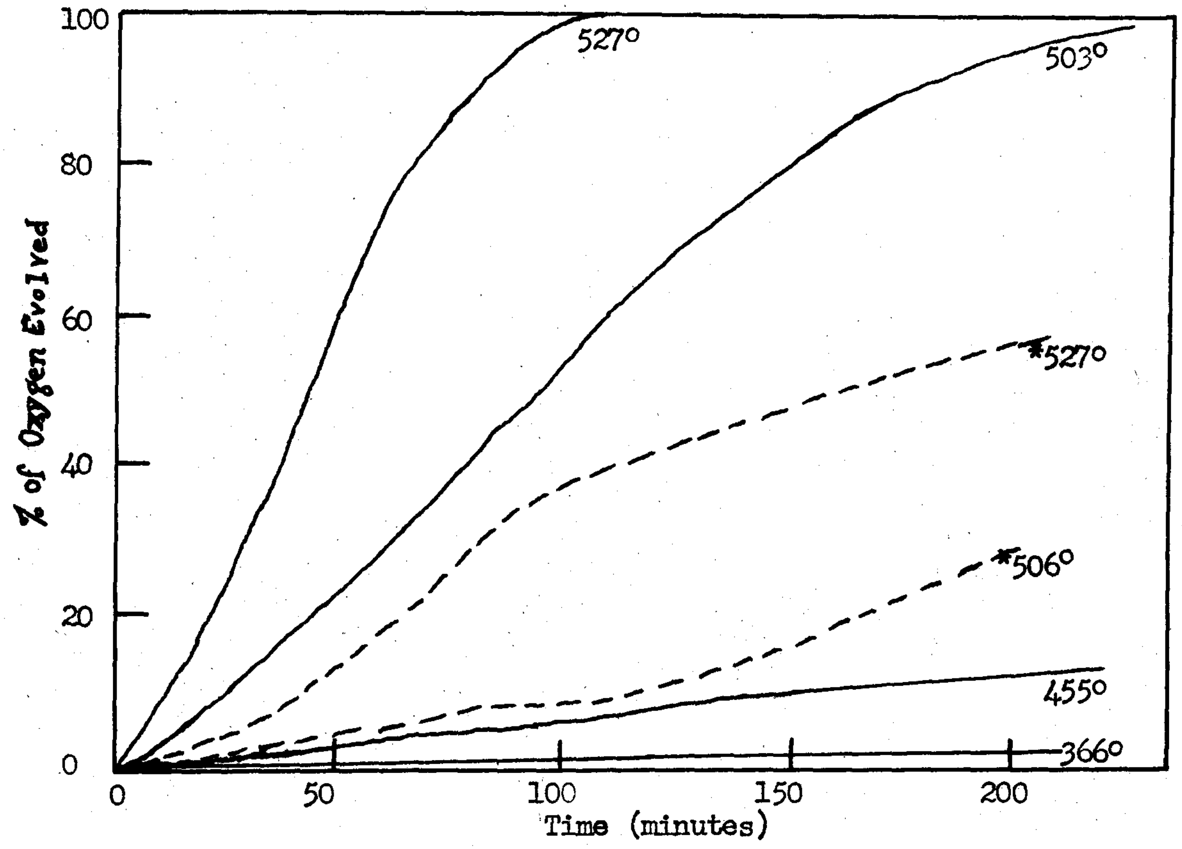

Figure 6. Decomposition of Pure $KClO_3$ at Various Temperatures (*Broken curves are from Glasner and Weidenfeld, J. Am. Chem. Soc., 74, 2465 (1952), Fig. 2.)

general shapes of the curves are similar, at 527° C. and at 503° C. the rates are faster than those of Glasner and Weidenfeld.

First order rate plots of the first parts of the decompositions at the four temperatures are shown in Figure 7. Specific reaction rate constants for the various temperatures were determined from slopes of these curves. They are summarized in Table VI.

Table VI

Specific Reaction Rate Constants for Decomposition of $KClO_3$ at Various Temperatures

Temperature	Specific Reaction Rate Constants
366°	1.38×10^{-5}
455°	2.13×10^{-4}
503°	5.53×10^{-3}
527°	1.33×10^{-2}

The Arrhenius equation plot (log k vs $\frac{1}{T}$) for the decomposition of $KClO_3$ is shown in Figure 11, curve 1. Calculation from the slope of the Arrhenius equation plot yields an apparent activation energy of 54 kcal. per mole.

Glasner and Weidenfeld (22), by comparing the times

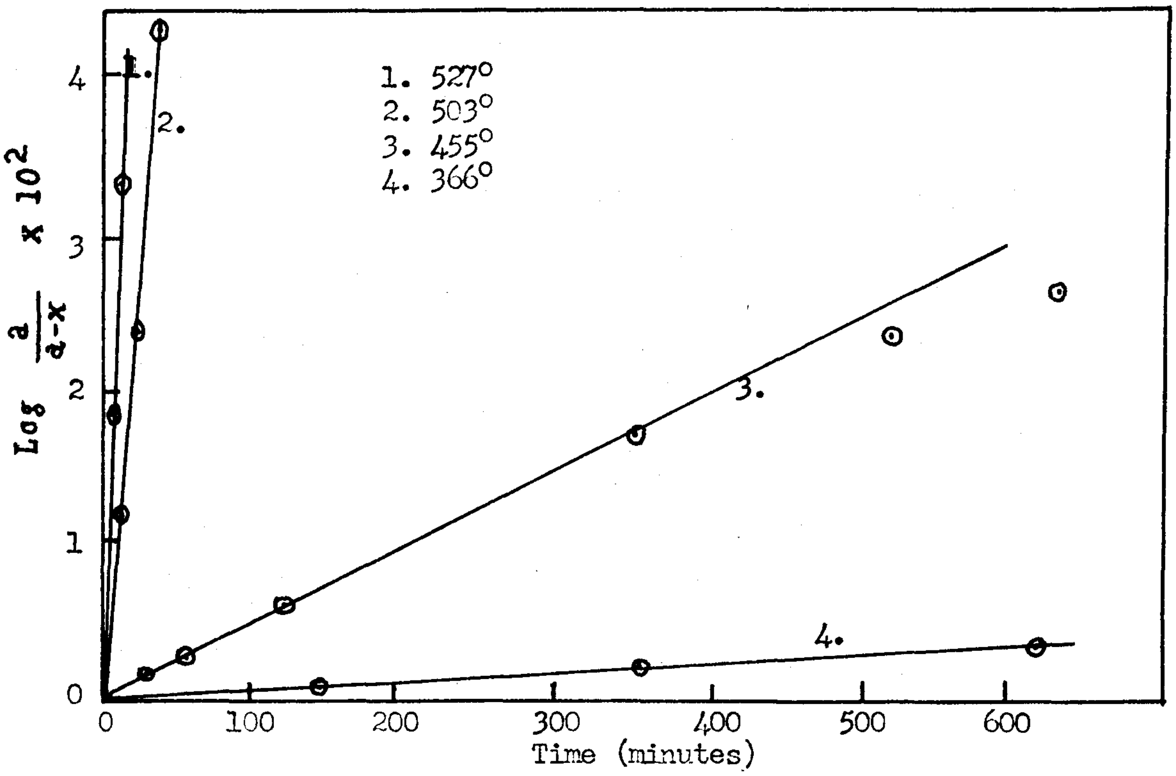

Figure 7. First Order Plots for Decomposition of Pure $KClO_3$

necessary to evolve 20% of the oxygen from potassium chlorate at various temperatures, also report an apparent activation energy of 54 kcal. per mole. Otto and Fry (19) showed that the decomposition of $KClO_3$ to chloride and oxygen is unimolecular; but the reaction becomes complex as it proceeds, due to the formation of perchlorate and due to the catalytic action of chloride on the perchlorate formation.

The first reaction to occur at the start of chlorate decomposition is evidently the formation of oxygen and chloride. First order plots of the first part of the reactions yield an activation energy that agrees with that already reported by Glasner and Weidenfeld. Therefore, the choice of first order kinetics for the determination of activation energies seems justified.

Decomposition of $KClO_3$ with manganese catalysts

Activation energies with manganese catalysts. Figures 8 and 9 are some of the decomposition curves copied on a smaller scale from curves recorded by the balance. Curves representing the decomposition of $KClO_3$ with a variety of manganese catalysts are shown. All reaction mixtures contained the same mole percentage of manganese.

The Fisher MnO_2 (curves 7, 8, 9, 10, and 11) is the most active manganese catalyst. Manganese metal (curves

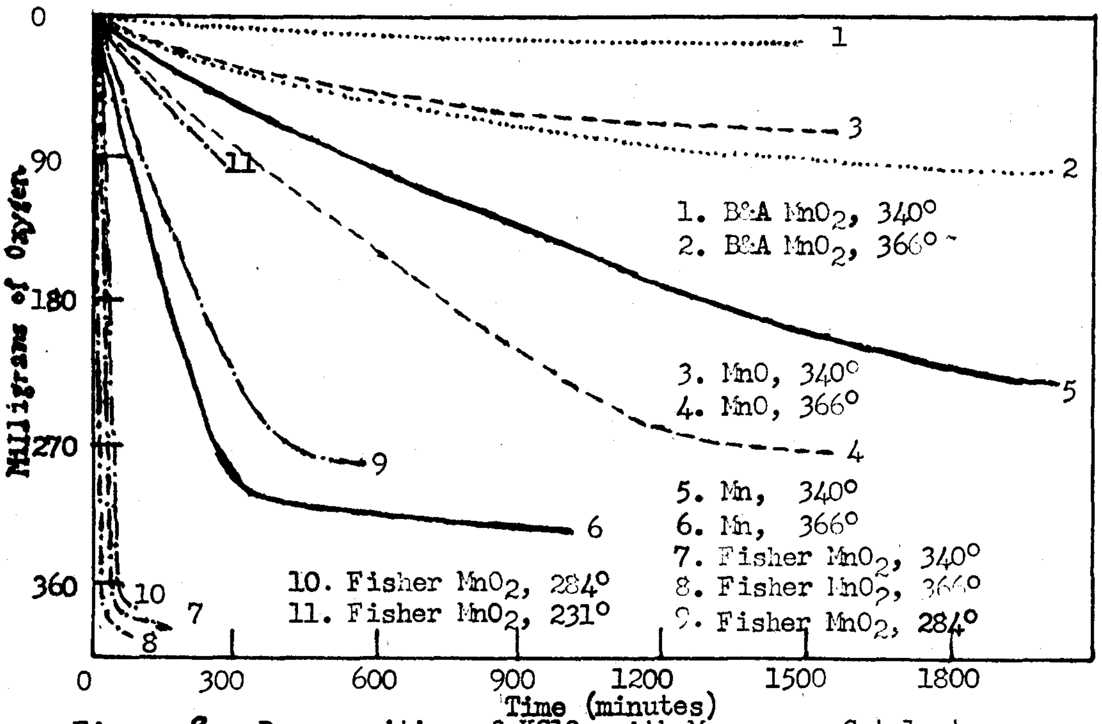

Figure 8. Decomposition of $KClO_3$ with Manganese Catalysts

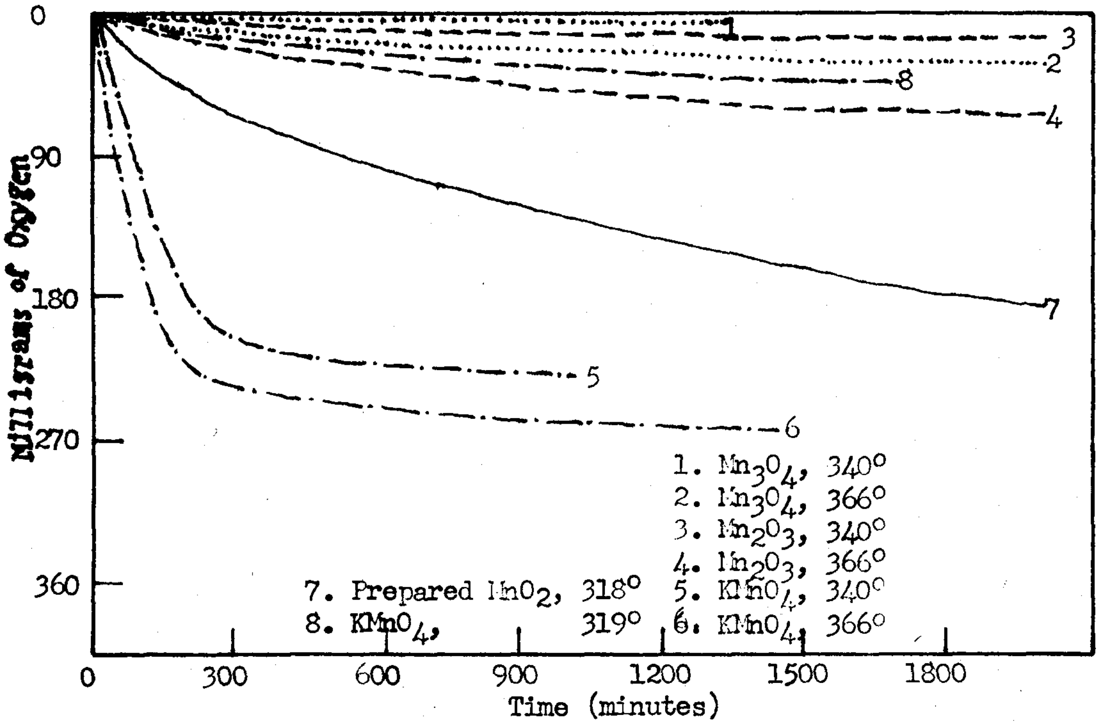

Figure 9. Decomposition of $KClO_3$ with Other Mn Catalysts

5 and 6, Figure 8) and $KMnO_4$ (curves 5 and 6, Figure 9) are also good catalysts, but the effect of temperature on their activities is greatly different. The Mn_3O_4 catalyst (curves 1 and 2, Figure 9) is the least active. It is observed that not all reactions liberated all the oxygen (392 milligrams) at a given temperature. This is in accordance with observations of previous workers (18,19).

The prepared MnO_2 (curve 7, Figure 9) was only run at one temperature, 318° C. At 318° C. its activity was greater than the activity of the B.&A. MnO_2 at 366° C. Its activity was greater than that of $KMnO_4$ at 319° C., but less than that of the Fisher MnO_2 at 284° C.

The manganese catalysts, in order of decreasing activity at 366° C. are: Fisher MnO_2, $KMnO_4$, Mn, MnO, B.&A. MnO_2, Mn_2O_3, and Mn_3O_4. At 340° C. the order is changed slightly, the positions of Mn and MnO being reversed.

First order rate plots were made from the decomposition curves. A sample of these plots is shown in Figure 10. The curves are for $KClO_3$ + B.&A. MnO_2 at three temperatures. Mixtures with Fisher MnO_2 catalyst were run at five temperatures. Mixtures with $KMnO_4$ were also run at five temperatures. All other mixtures were run at only two temperatures. The first order specific reaction rate constants for the various reactions with manganese catalysts are summarized in Table VII.

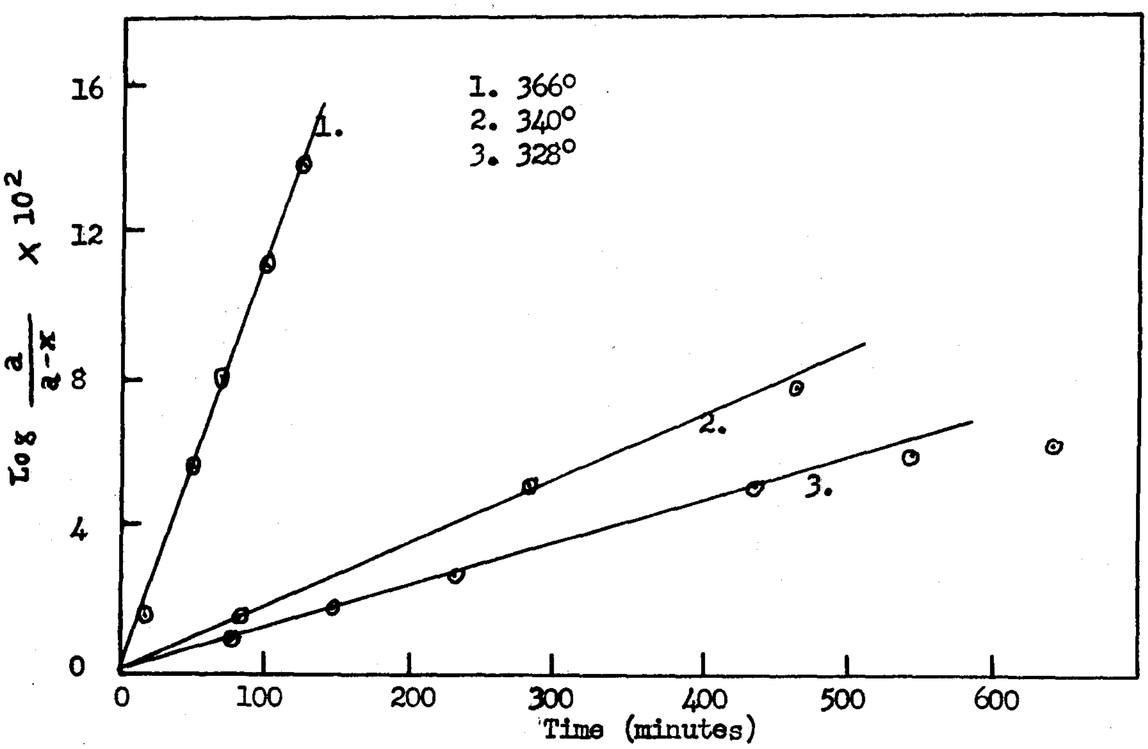

Figure 10. First Order Plots for Decomposition of $KClO_3$ with MnO_2

Table VII

Specific Reaction Rate Constants for Decomposition of $KClO_3$ with Mn Catalysts

Catalyst Used	Temperature C°	Reaction Rate Constant
MnO_2, B.&A.	366	1.56×10^{-3}
	340	1.69×10^{-5}
	328	2.04×10^{-5}
MnO_2, Fisher	366	2.04×10^{0}
	340	6.25×10^{-1}
	312	4.98×10^{-2}
	284	1.79×10^{-3}
	231	1.72×10^{-4}
$KMnO_4$	377	1.19×10^{-2}
	366	4.77×10^{-3}
	340	2.93×10^{-3}
	329	8.92×10^{-4}
	319	9.82×10^{-5}
Mn	366	7.45×10^{-3}
	340	4.33×10^{-4}
MnO	366	7.88×10^{-4}
	340	1.45×10^{-4}
Mn_2O_3	366	1.62×10^{-4}
	340	2.30×10^{-5}
Mn_3O_4	366	5.98×10^{-5}
	340	1.75×10^{-5}

Figure 11 is the result of plotting the logarithm of the reaction rate constants versus the reciprocal of the temperatures on the absolute scale. Curve 1 is the Arrhenius plot for pure $KClO_3$ referred to earlier. Curves 2, 3, and

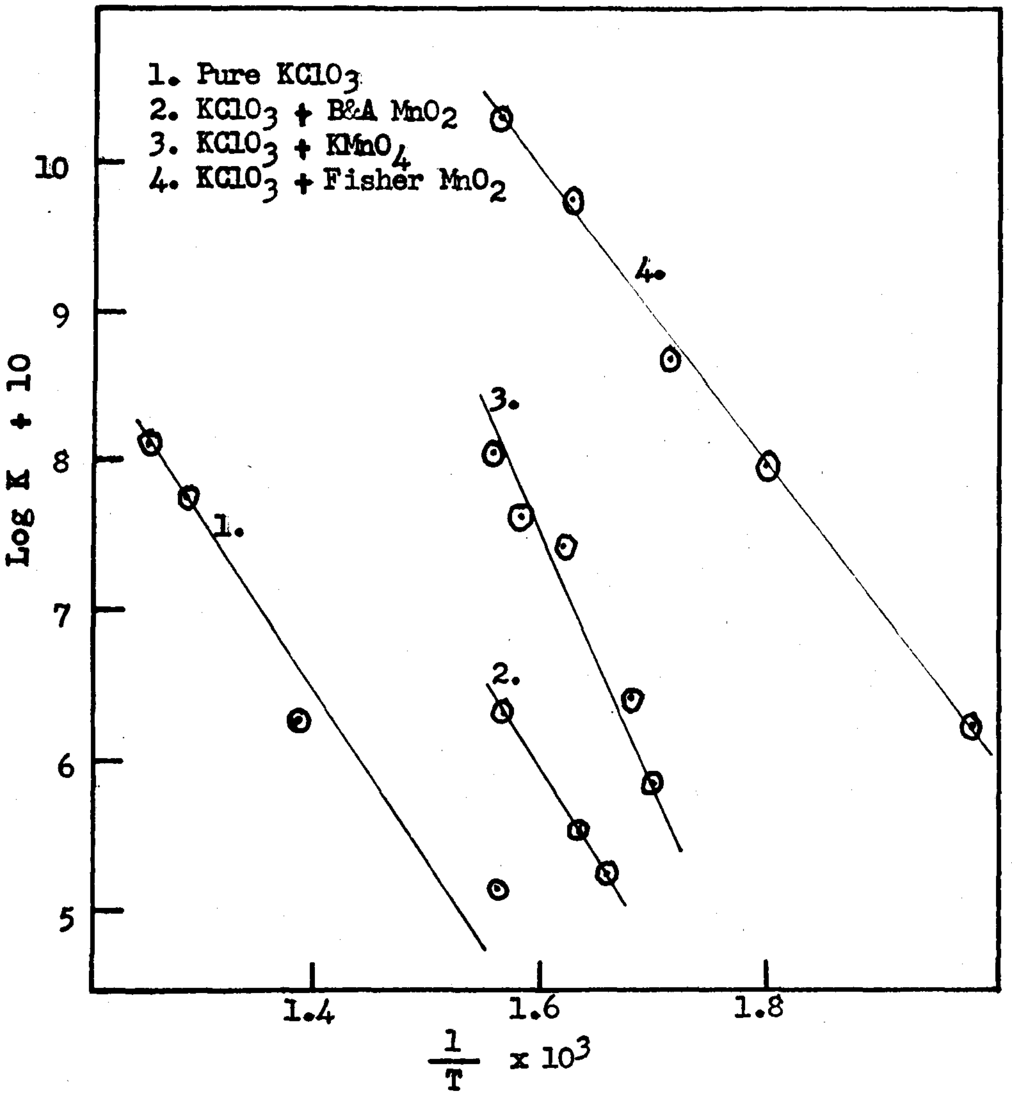

Figure 11. Arrhenius Equation Plots of Decompositions

4 are for runs with B.&A. MnO_2, $KMnO_4$, and Fisher MnO_2, respectively. The Fisher MnO_2 mixture and the B.&A. MnO_2 mixture are represented by the Arrhenius law exactly, over the range of temperatures used. The points, for the pure $KClO_3$ curve and for $KClO_3$ with $KMnO_4$, do not all fall exactly on the straight line, but the series of points approach straight lines. This close accord with the Arrhenius law also supports the use of first order kinetics in obtaining reaction rate constants.

Activation energies for all other mixtures were obtained by calculation from the rate constants at two temperatures. Observation of curves 1 and 3, Figure 11, shows that activation energies obtained from pairs of points are not always the same. Probably plots of points at several temperatures are more accurate. Therefore, values obtained are called only apparent activation energies.

A summary of the apparent activation energies for the decomposition of $KClO_3$ with the various manganese catalysts is given in Table VIII.

It is interesting that decompositions with Mn, oxidation state 0, and with $KMnO_4$, oxidation state 7, exhibit the highest activation energies. Both of these catalysts are quite active as was shown in Figures 8 and 9. On the other hand, Mn_3O_4, the least active catalyst, exhibits the

Table VIII

Summary of Apparent Activation Energies for Reactions with Manganese Catalysts

Catalyst Used	Number of Temperatures Run	Oxidation State of Mn	Apparent Activation Energy (kcal./mole)
Mn	2	0	85
MnO	2	2	50
Mn_3O_4	2	2-2/3	37
Mn_2O_3	2	3	58
MnO_2, Fisher	5	4	45
MnO_2, B.&A.	3	4	52
$KMnO_4$	5	7	77
None (pure $KClO_3$)	5	---	54

lowest activation energy. Fisher MnO_2, the most active catalyst, however, exhibits a low activation energy.

Activation energies for decomposition of $KClO_3$ with manganese catalysts were lower for those catalysts with manganese in an intermediate oxidation state than for catalysts with manganese in very high or very low valences. In Mn_3O_4 manganese exists in more than one oxidation state, 2 and 4, and possible 2 and 3, according to Myers and Kanters (47). The fact that the decomposition rate was slowest for this catalyst, in spite of the low activation energy, is probably due to the high temperature (1000° C.) employed in preparation of the Mn_3O_4. High temperature often results in a sintering of the surfaces of catalyst particles (52).

Fate of the manganese catalysts. Table IX is a summary of the results of analyses for manganese and for permanganate in the residues from the decomposition of $KClO_3$ with manganese catalysts. The catalysts used, temperatures of the runs, and the total times of heating are in the first three columns. The percentage of oxygen evolved shows how far each reaction progressed before slowing to approximately 1 milligram of oxygen per hour. The fifth column shows the ratio of oxygen atoms to manganese atoms in the insoluble portions of the residues. The last column shows the fraction of the manganese that was extracted from the residues as permanganate.

Absorption spectra of some of the slightly pink solutions were run to reconfirm that the pink solutions from the residues actually did contain permanganate. Figure 12 contains samples of absorption spectra of these solutions. Curve 1 is the absorption spectrum of a solution of $KMnO_4$ of approximately the same concentration as the other solutions. Curves 2, 3, and 4 are absorption spectra of

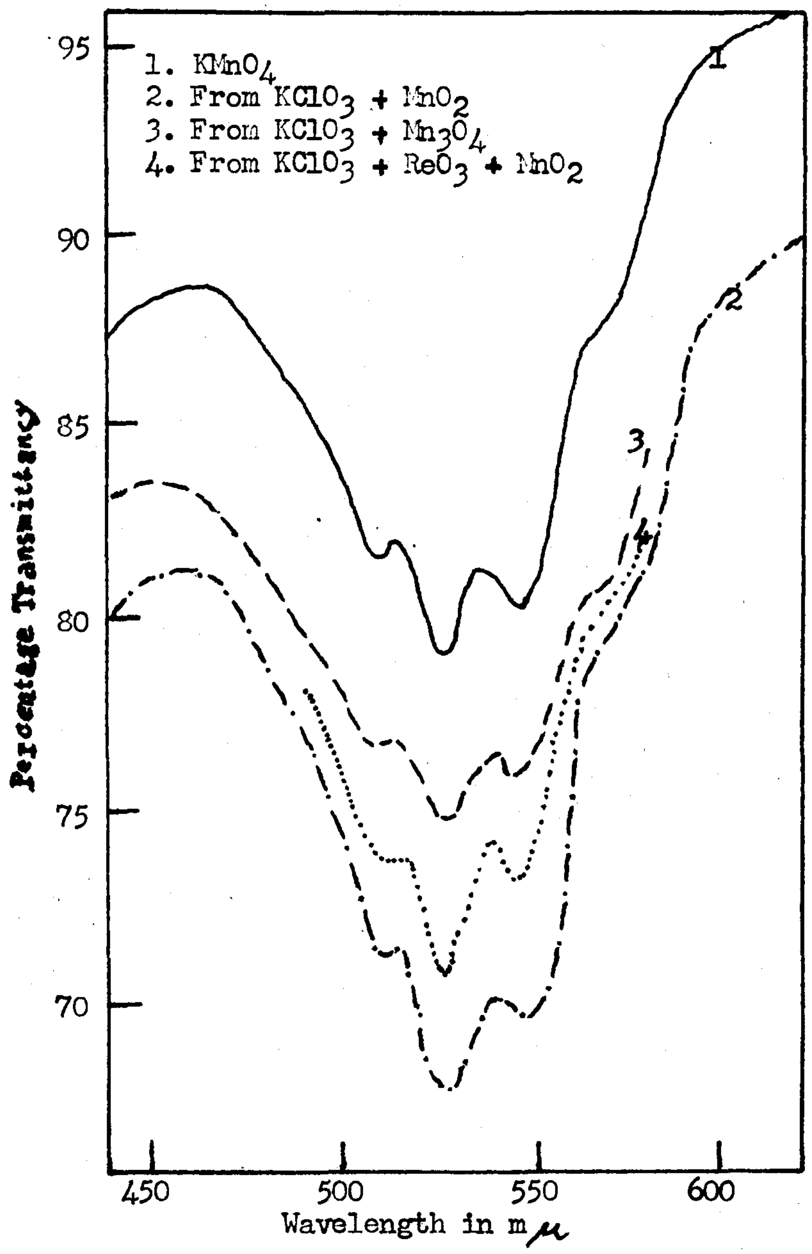

Figure 12. Absorption Spectra of Solutions Containing Mn

solutions containing the soluble portions of reaction residues from $KClO_3$ decomposition with MnO_2, Mn_3O_4, and with a mixture of ReO_3 MnO_2, respectively. The fact that all the curves exhibit the three characteristic minima at 505 mμ, 525 mμ, and 548 mμ leaves no doubt that all contain permanganate.

Table IX

Analysis of Decomposition Residues, Showing Fate of Manganese Catalysts

Catalyst	Temperature of Run	Time (min.)	% Oxygen Evolved	Formula of Residue Oxide	% Mn in $KMnO_4$
Mn	366°	1000	83.4	$MnO_{1.2}$	0.4
MnO	366°	2622	76.5	$MnO_{1.8}$	Trace
	340°	1478	19.2	$MnO_{1.7}$	0.1
Mn_2O_3	366°	2620	21.0	$MnO_{1.7}$	0.3
	340°	276	1.7	$MnO_{1.8}$	0.2
	340°	2835	7.7	$MnO_{1.6}$	0.8
MnO_2,B.&A.	366°	4440	27.0	$MnO_{1.7}$	0.1
	366°	2400	25.0	---	0.3
	340°	1311	4.1	$MnO_{2.0}$*	0.0
MnO_2,Fisher	366°	75	99.0	$MnO_{1.3}$	Trace
	340°	92	99.0	$MnO_{1.9}$	0.0
$KMnO_4$	366°	180	42.2	$MnO_{1.5}$	13.0
	366°	1518	67.8	$MnO_{1.7}$	14.0
	340°	1265	60.8	$MnO_{2.0}$	24.0

*Analyzed by bismuthate method and colorimetrically.

Inspection of column 4, Table IX, reveals a series of oxides with manganese to oxygen ratios from $MnO_{1.2}$ to $MnO_{2.0}$. The method of analysis of these small samples was not accurate enough to make a clear distinction between the small differences in ratios. However, the column as a whole indicates that most of the manganese, regardless of its oxidation state at the start, ends up with an intermediate oxidation state of 3 to 4. Manganese metal and MnO were oxidized. $KMnO_4$ was reduced.

The last column, Table IX, indicates that in most cases a detectable or measurable fraction of the manganese could be extracted from the residues as permanganate. Permanganate was found in the residues in spite of the fact that $KMnO_4$ decomposes at 240° C., whereas these reactions were carried out at 340° and 366° C. It is significant that when $KMnO_4$ was used as catalyst, as much as 14% of the manganese could be extracted from the residue, even after heating for 21 hours at a temperature 126° C. above the decomposition point of $KMnO_4$. From the residues from the Fisher MnO_2 reactions, little or no permanganate could be extracted. However, when this catalyst was used, the decomposition of chlorate was complete, and any permanganate present may have decomposed before the reactions were stopped. When a mixture with Fisher MnO_2 was heated only 3 minutes, the water extract of the residue contained permanganate.

The reaction mixtures usually appeared light grey-brown with a pink tint. They usually were partially melted at 366° C. At 340° C. they remained unmelted but always appeared to have sintered. Occasionally a residue appeared to have a green tint. This possibly indicated the presence of a trace of manganate, although the decomposition temperature of manganate is only 190° C. When water was added to any green tinted residue, pink solutions resulted, showing that any manganate present underwent disproportionation to yield $KMnO_4$ in solution.

These results show that the oxidation state of manganese changes during the catalytic decomposition of $KClO_3$. The presence of permanganate in the residues makes it probable that the catalytic action involves oxidation of the manganese to a high oxidation state with a subsequent decomposition of the intermediate to yield oxygen.

Table X is a summary of the results of analyzing the residues of some mixtures for chlorate, perchlorate, and chloride from runs at a given temperature, but carried out over different periods of time. This indicates something of the rate at which the composition of the reaction mixtures was changing during oxygen evolution. The time, column 2, refers to total time the reaction mixtures were heated. The % O_2 is the total fraction of the 392 mg. of oxygen liberated from the 1.000 g. samples of $KClO_3$. Chlorate, perchlorate, and chloride are reported as the percentage of total Cl ending up in $KClO_3$, $KClO_4$, and KCl.

Table X

Analysis of Various Decomposition Residues, Showing Rates of Variation in Composition at Constant Temperature

Run	Time (hours)	% O_2	% of Total Cl		
			$KClO_3$	$KClO_4$	KCl
			(With MnO_2 catalyst, 366° C.)		
1	28.2	28.0	19.3	35.1	39.8
2	74.0	27.0	26.2	36.4	36.4
3†	67.8	25.0	4.3	65.8*	29.8
			(With MnO catalyst, 366° C.)		
4	2.1	5.3	88.8	1.4	1.1
5	5.9	20.9	73.7	1.3	11.6
6	43.7	76.5	5.6	15.7	92.8
			(With $KMnO_4$ catalyst, 366° C.)		
7	3.0	42.2	34.7	19.0*	46.3
8	25.2	67.8	10.5	15.0*	74.2
			(With Mn metal catalyst, 366° C.)		
9	2.1	56.8	17.1	41.2	41.7
10	16.7	83.4	4.5	32.8	62.7
			(With Mn_2O catalyst, 340° C.)		
11	4.6	1.7	93.1	4.1*	2.1
12	39.8	5.7	83.4	5.1*	9.3

†Interrupted run.

*Calculated by difference.

When MnO_2 was the catalyst at 366° (runs 1 and 2), a 28 hour run and a 74 hour run produced residues with similar percentages of perchlorate. (Run 3 received special treatment, as is explained later.) When MnO (runs 4 and 5) was used as catalyst at 366° C., residues from a 2 hour run and a 5 hour run contained nearly the same percentages of perchlorate, although a greater fraction of the $KClO_3$ was decomposed in the 5 hour run. However, a 40 hour run (run 6) yielded an increase in perchlorate with a corresponding decrease in chlorate.

When $KMnO_4$ was used as catalyst at 366° C. (runs 7 and 8), a 3 hour and a 25 hour run produced residues with similar percentages of perchlorate. Residues from runs with manganese metal (runs 9 and 10) also yielded residues with similar perchlorate concentration after 2 hours and 16 hours, respectively. With Mn_2O_3 as catalyst at 340° C. (runs 11 and 12), residues from runs for 5 hours and for 40 hours also showed a somewhat constant perchlorate concentration.

These results indicate that a somewhat constant percentage of perchlorate remains for considerable periods of time in a given reaction mixture at a given temperature during the decomposition of $KClO_3$. In all these cases some chlorate remained in the reaction mixtures even though the oxygen evolution was practically stopped when the reaction tubes were taken from the furnace. Not enough data is available for complete interpretation of these results, but the complexity of the decomposition of potassium chlorate is further illustrated.

Results of some special experiments with MnO_2. Some special experiments were carried out on the decomposition of $KClO_3$ with B.&A. MnO_2 as catalyst. A mixture was decomposed at 366° C. until no more than 1 milligram of oxygen was liberated per hour. The balance recorder was stopped and the reaction tube was taken from the furnace and cooled. The residue was then carefully ground in an agate mortar and replaced in the reaction tube. The recorder was again turned on.

Figure 13, curve 3, is the decomposition curve in question. The point marked x is the point of interruption of the run. Curve 2 is uninterrupted, but otherwise treated in exactly the same manner. The two curves indicate the reproducibility of similar runs. Curve 1 is the decomposition of pure $KClO_3$ at 366° C. for comparison.

It is observed that no more oxygen was evolved after the interruption for grinding the residue. However, the analysis of the residues from the two runs shows a quite different composition. The analysis for these two runs

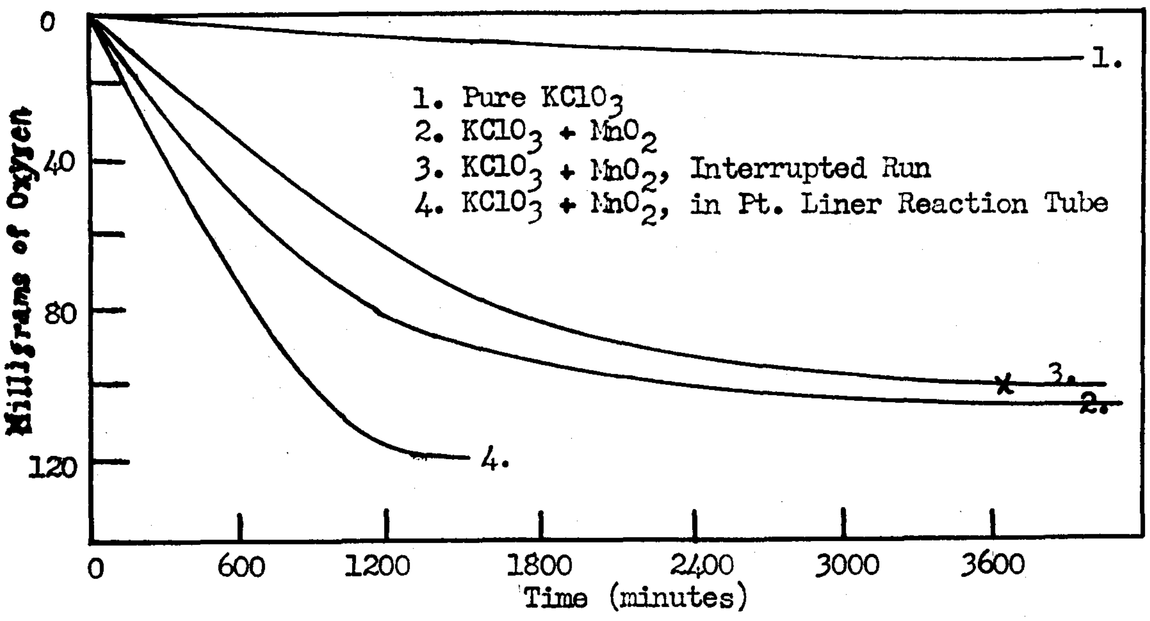

Figure 13. Decomposition of $KClO_3$ with MnO_2, 366°

was included in Table X, runs 2 and 3. It is observed that the residue from the interrupted run contained 66% $KClO_4$. However, residues from runs 1 and 2, both uninterrupted, contained about 36% $KClO_4$. This experiment indicates that the physical state of the solid reaction mixtures influenced the rate of perchlorate formation. The grinding of the residue evidently broke down barriers that allowed a reaction to continue, even though no more oxygen was evolved.

One decomposition curve for $KClO_3$ with MnO_2 was run in a platinum lined reaction tube since Mathers and Alred (18) reported that glass surfaces affect the decomposition. The result of this decomposition is shown in Figure 13, curve 4. It is observed that in a platinum liner the decomposition was faster than that in a pyrex glass tube. The rate of oxygen evolution fell off more abruptly when the platinum liner was used, however. The results of this experiment prove that in this case a glass surface did not cause as rapid decomposition of $KClO_3$ as did a platinum surface.

Decomposition of $KClO_3$ with rhenium catalysts

Activation energies with rhenium catalysts. Figures 14 and 15 show the rates of decomposition of $KClO_3$ with the various rhenium catalysts at 340° C. and 366° C.

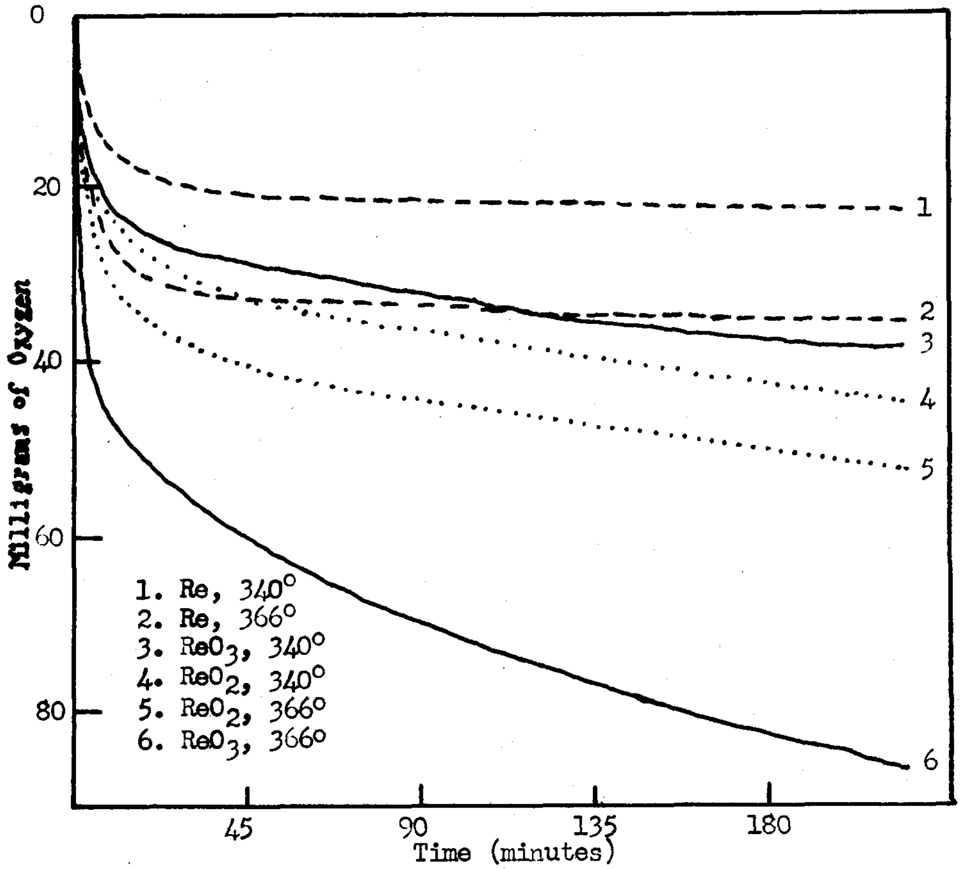

Figure 14. Decomposition of $KClO_3$ with Re Catalysts

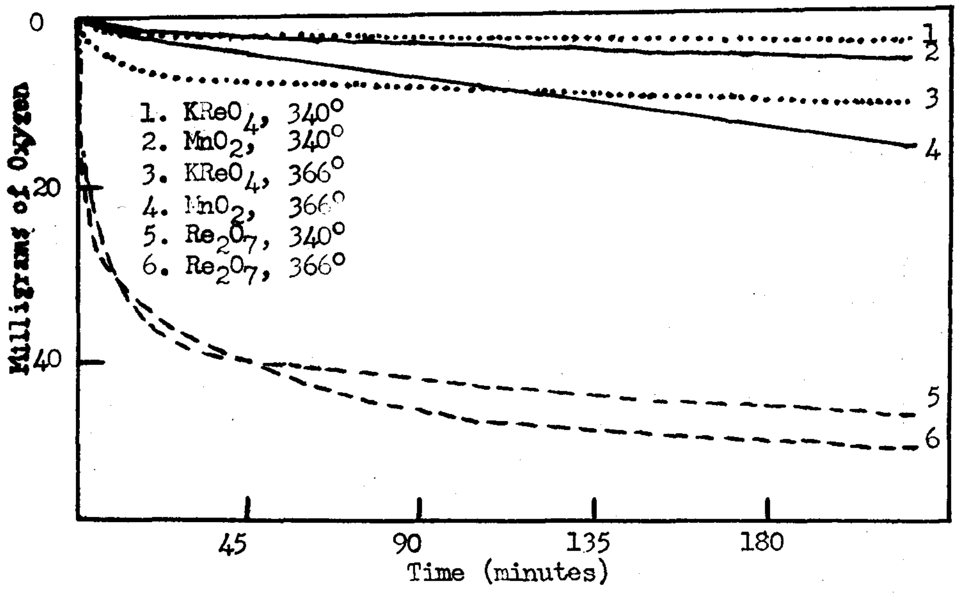

Figure 15. Decomposition of $KClO_3$ with Re, Compared with MnO_2

The curves were reproduced on a smaller scale directly from chart paper recording from the automatic recording balance. All the curves are of a similar type. They exhibit a rapid evolution of oxygen for a few minutes. Then the reactions abruptly slow to from 0 to a few milligrams of oxygen per hour. In all cases increased temperature caused a greater total weight of oxygen to be liberated. Mixtures containing ReO_3 (curves 3 and 4, Figure 14) are the only exception. They exhibit a continued slow catalysis after the break in oxygen evolution.

Curves 2 and 4 (Figure 15) are parts of curves for the decomposition of $KClO_3$ with B.&A. MnO_2, included for comparison. The slopes of the MnO_2 curves show a much more gradual oxygen evolution from the start of the reactions. The complete manganese curves shown elsewhere (Figure 8) revealed that the manganese catalysts maintained catalytic activity over extended periods of time with an over all higher yield of oxygen at the same temperatures.

The nature of the chlorate decomposition curves with rhenium catalysts made it difficult to obtain specific reaction rate constants for the beginning of the reactions. The recording balance could not accurately plot the rapid rates of the first few minutes of the decompositions. Little contrast in slopes of the decomposition curves occurred during the comparatively few minutes of oxygen evolution. The similarity of curves obtained from decompositions of the same mixtures at two temperatures indicated low activation energies for all the reactions that occurred.

In spite of the inaccuracies involved, first order rate plots were made for decompositions of $KClO_3$ with the rhenium catalysts. Rate constants were then obtained from the slopes of these curves. Figure 16 is a sample of the first order plots. The curves are for the decompositions of $KClO_3$ with Re and with ReO_2 catalysts, respectively. The temperature of the runs were 340° and 366° C. The broken lines indicate the slopes used for obtaining rate constants for the first parts of the reactions. A slight error in these slopes affects the values of the rate constants appreciably. Therefore, rate constants and activation energies calculated for decomposition of $KClO_3$ with rhenium catalysts are not considered to be very accurate.

Table XI is a summary of the specific reaction rate constants for the decomposition of $KClO_3$ with the various rhenium catalysts at two temperatures.

From the constants at the two temperatures shown in Table XI apparent activation energies for the reaction were calculated by the Arrhenius equation. The results of these calculations are summarized in Table XII.

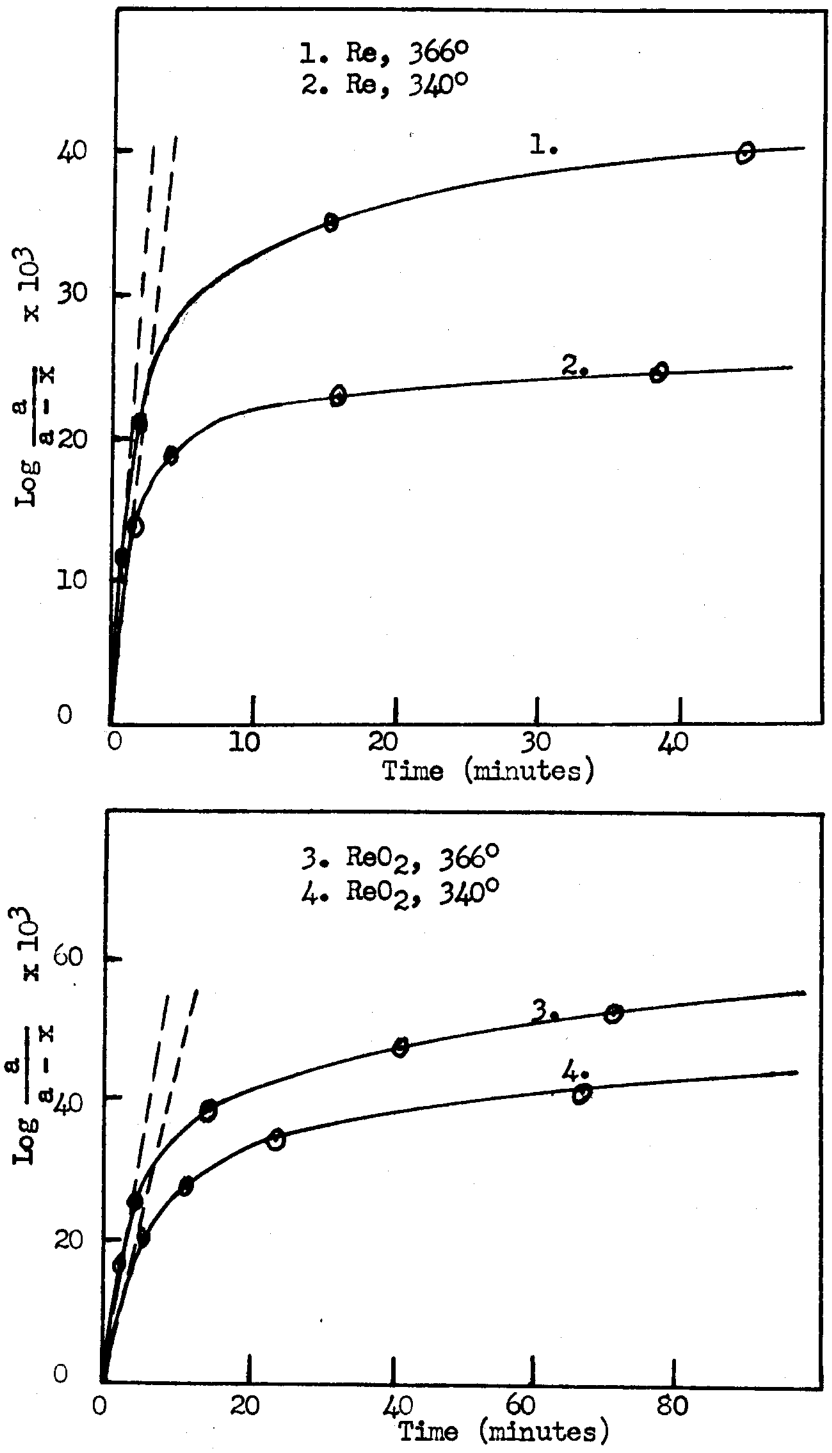

Figure 16. First Order Plots for Decomposition of $KClO_3$ With Re Catalyst and With ReO_2 Catalyst

Table XI

Specific Reaction Rate Constants for Decomposition of $KClO_3$ with Rhenium Catalysts

Catalyst Used	Temperature C°	Reaction Rate Constants
Re	366	2.6×10^{-2}
	340	1.9×10^{-2}
ReO_2	366	1.2×10^{-4}
	340	9.5×10^{-5}
ReO_3	366	2.7×10^{-4}
	340	1.2×10^{-4}
Re_2O_7	366	---
	340	---
$KReO_4$	366	3.2×10^{-3}
	340	5.1×10^{-4}

Table XII

Summary of Apparent Activation for Reactions with Rhenium Catalysts

Catalyst Used	Oxidation State	Apparent Activation Energy (kcal./mole)
Re	0	9
ReO_2	4	6
ReO_3	6	23
Re_2O_7	7	--
$KReO_4$	7	54
(Pure $KClO_3$)	---	54

As was stated earlier, the activation energies in Table XII cannot be considered very accurate. That the values are much lower than the corresponding values with manganese catalysts can be concluded with confidence, however. As with the manganese catalysts, the lowest value occurs for decompositions with rhenium in an intermediate oxidation state. It is observed that the decomposition of $KClO_3$ with $KReO_4$ has the same activation energy as pure $KClO_3$, itself. This compound exhibited the least catalytic activity of any of the rhenium catalysts, as was shown in Figure 15.

Fate of rhenium catalysts

Table XIII is a summary of the results of analyses of residues from the decomposition of $KClO_3$ with rhenium catalysts. The effect of temperature and total time of heating is shown. In general, the 366° C. temperature produced the highest yield of $KClO_4$ in the reaction residues. Runs with ReO_3 as catalysts are exceptions, however. In this case the 340° C. run gave the highest yield of $KClO_4$. It should be noted that this was the only 340° C. run carried out for a longer period of time than a corresponding 366° run. Thus, the time of heating affects the composition of the residues in a way not completely measured by the rate of oxygen evolution.

Table XIII

Analysis of Various Residues, After Decomposition of $KClO_3$ with Rhenium Catalysts

Run	Temperature C°	Time (min.)	% of Total Cl			Wt. O_2 (from chart)	Wt. O_2 (calc. from chloride)
			$KClO_3$	$KClO_4$	KCl		
(With Re metal catalyst)							
1	366	1080	83.7	4.3	12.2	43 mg.	46 mg.
2	340	188	91.1	1.2	6.2	25	24
(With ReO_2 catalyst)							
3	366	1820	61.3	8.6	27.3	107	107
4	340	936	79.7	7.3	17.1	69	67
(With ReO_3 catalyst)							
5*	366	2740	14.1	14.3	71.2†	278	280
6	366	1680	45.2	14.6	37.2	185	162
7	340	2760	65.3	29.4	6.1	118	116
(With Re_2O_7 catalyst)							
8	366	892	86.7	11.4	9.1	60	35
9	340	172	85.7	4.7	9.4†	50	30
(With $KReO_4$ catalyst)							
10	366	1000	77.7	7.9	14.5	29	26
11	340	350	96.1	3.7	0	5	14

*ReO_3 contained trace of Mn.

†Calculated by difference.

Rhenium heptoxide has a melting point of 220° C. and sublimes at 450° C. The comparatively low sublimation point for this oxide made it imperative to insure that the weight loss recorded by the automatic recording balance was, indeed, due to oxygen evolution only and not due to loss of catalyst by vaporization. Therefore, all $KClO_3$ mixtures with rhenium catalysts were run in long reaction tubes, extending several centimeters above the furnace. In no case was any deposit of any rhenium compound observed to condense on the cooler portion of the tubes.

The analyses of residues gave a further check on whether or not rhenium catalysts were lost by vaporization during the reactions. In each case the weight of oxygen, corresponding to the amount of chloride formed in the reaction, was calculated. This weight of oxygen was compared with the weight read from the automatic record. The last two columns (Table XIII) show the results of this check. There is close agreement in all cases except for runs 8 and 9, the Re_2O_7 runs. In these runs significantly more weight loss was recorded than was accounted for by the amount of chloride in the residues. In spite of the fact that no deposit was seen to collect on the cooler portion of the reaction tubes, it was necessary to conclude that part of the Re_2O_7 catalyst escaped during the reactions. For all other runs with other rhenium catalysts there was no weight loss except that of oxygen.

It was stated earlier that during the grinding of the Re, ReO_3, and Re_2O_7 catalysts with $KClO_3$, a faint chlorine-like odor was observed. A check was made to see if chlorine products were liberated during the decomposition runs. A pyrex tube extending into an electric furnace was connected to a small liquid trap immersed in an acetone-dry ice bath at -80° C. A mixture of $KClO_3$ with Re as catalyst was placed in the pyrex tube and heated at 340° C. for 1 hour. Only a fine film of moisture collected in the trap. No chlorine-like odor was observed in the trap. The trap was washed with a few drops of water. One drop of 0.08 N KOH gave a phenolphthalein end point showing no chlorine or oxides of chlorine were in the trap. This check further proved that the balance was recording only the loss of oxygen during the decomposition of $KClO_3$ with the rhenium catalysts.

The residues from all the decompositions of $KClO_3$ with the various rhenium catalysts were partly or wholly melted when removed from the furnace at 366° C. At 340° C. the residues appeared to be sintered. Evidently low melting point mixtures were produced.

All the residues were completely soluble in water with the exception of runs with ReO_2. Residues from these runs contained an insoluble grey substance weighing about 10% of the weight of the ReO_2. The original analysis of the ReO_2 catalyst showed it to be only 85% pure. The method of preparation of the ReO_2 was such that impurities from the Re, impurities from the rhenium dioxanate intermediate, and impurities from the ReO_3 would be left in this oxide. That the grey insoluble portion left after water extraction contained no rhenium was proved by the fact that it would not dissolve in 30% H_2O_2 as all rhenium oxides do (53). Of the catalysts used only Re_2O_7 and $KReO_4$ are soluble in water. All the other catalysts were converted to a soluble form during the decomposition reactions.

Absorption spectra in the ultraviolet were determined with a Beckman D.U. spectrophotometer on the solutions of the residues that contained rhenium. Table XIV is a summary of the sources of the solutions for which absorption spectra were run.

The absorption spectra for solutions of Table XIV are shown in Figure 17. Numbers of the curves refer to solution numbers in Table XIV. Curve 1 is the ultraviolet absorption spectrum of 0.0017 M standard perrhenate. Curve 9 is a 0.0245 M perrhenate curve reproduced from data of Maun (45). The shapes of curves 1 and 9 are similar. There is only a small shift in position for a 100 fold change in concentration. Therefore, quantitative determinations for perrhenate were not possible.

Curve 2 is an absorption spectrum of a prepared solution of a chloride, chlorate, and perchlorate mixture.

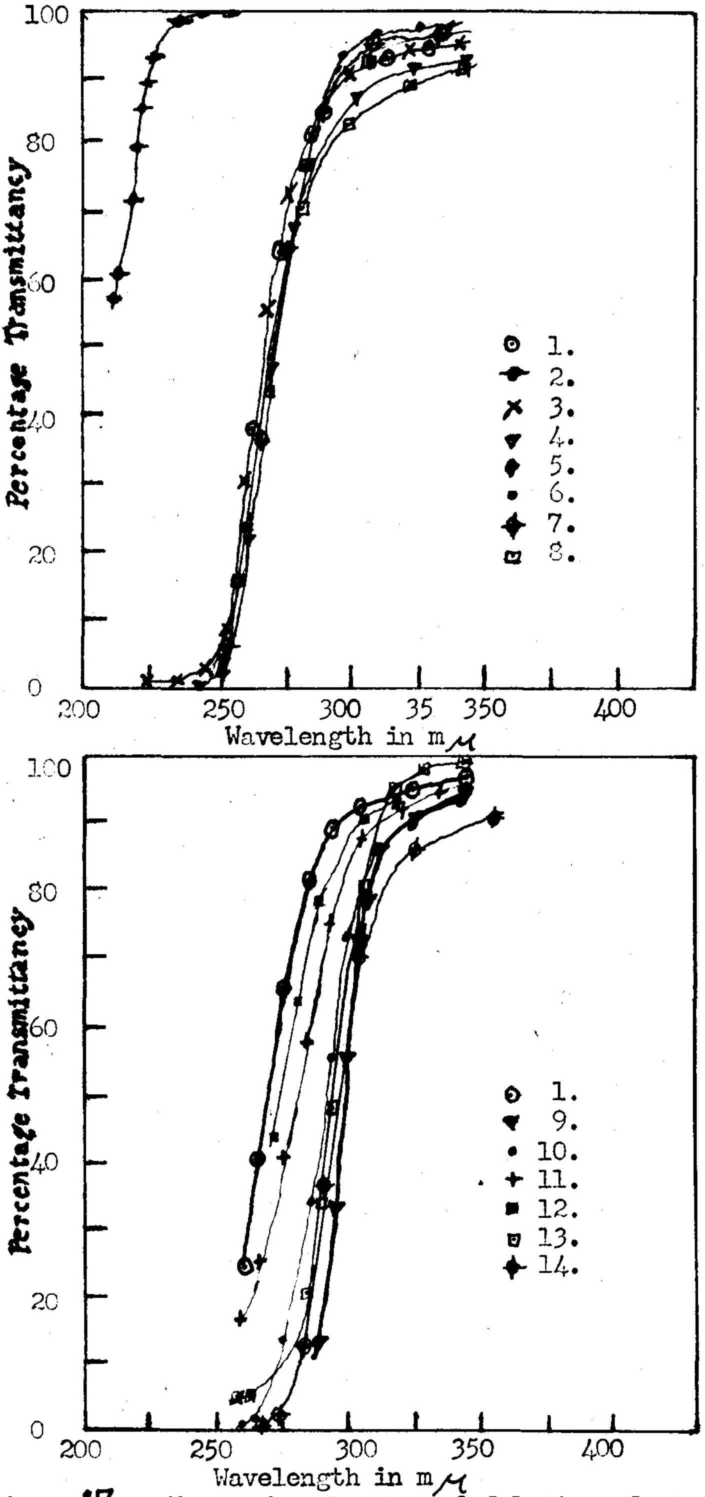

Figure 17. Absorption Spectra of Solutions Containing Re

Table XIV

Sources of Solutions for Perrhenate Absorption Spectra[a]

Solution[b]	Source
1	Standard $HReO_4$, 0.0017 M
2	0.1 g. KCl + 0.1 g. $KClO_3$ + 0.1 g. $KClO_4$ in 50 ml. H_2O
3	Residue from $KClO_3$ + ReO_2, 366°
4	Residue from $KClO_3$ + Re, 366°
5	Residue from $KClO_3$ + ReO_3, 366°
6	Residue from $KClO_3$ + ReO_3, 366° (repeat)
7	Residue from $KClO_3$ + ReO_3 MnO_2, 366°
8	Residue from $KClO_3$ + $KReO_4$, 366°
9[c]	0.0245 M $HReO_4$
10	Residue from $KClO_3$ + ReO_2, 340°
11	Residue from $KClO_3$ + ReO_3, 340°
12	Residue from $KClO_3$ + $KReO_4$, 340°
13	Residue from $KClO_3$ + Re_2O_7, 366°
14	Residue from $KClO_3$ + Re_2O_7, 340°

[a] Absorption spectra shown in Figure 17.

[b] Solution number same as curve number in Figure 17.

[c] From Maun, "Investigations in Chemistry of Rhenium," Ph. D. Thesis, California Institute of Technology, 1949. (Unclassified A.E.C. Report, N-P 1378).

The position of absorption proves that these salts do not interfere with the perrhenate absorption band. Each of the water solutions of the residues from the decomposition of $KClO_3$ with rhenium catalysts exhibits the perrhenate absorption spectrum. Since all the rhenium from each run was soluble, the conclusion can be made that all the rhenium is converted to perrhenate during decomposition of $KClO_3$ regardless of its oxidation state at the beginning of the reaction.

It was shown that rhenium oxides readily decompose $KClO_3$ for only a few minutes and then the catalytic activity stops. It was shown that all the rhenium was in the form of perrhenate at the end of each reaction. Evidently the catalytic activity is associated with the changing of the oxidation state of the rhenium. These facts have a significant bearing on the interpretation of the catalytic activity of manganese or the decomposition of $KClO_3$.

Decomposition of $KClO_3$ with rhenium and manganese mixtures

An abnormal rate of $KClO_3$ decomposition was observed for one run in which ReO_3 was used as catalyst at 366° C. The decomposition curve for this run is curve 1, Figure 18. Curve 2 represents the normal decomposition with this catalyst. It was noted that the $KClO_3$-ReO_3 mixture had been ground in a mortar in which manganese metal had just been ground. The abnormal decomposition was, therefore, due to contamination with manganese. Experiments were then carried out to see if manganese acts as a promotor on rhenium catalysts.

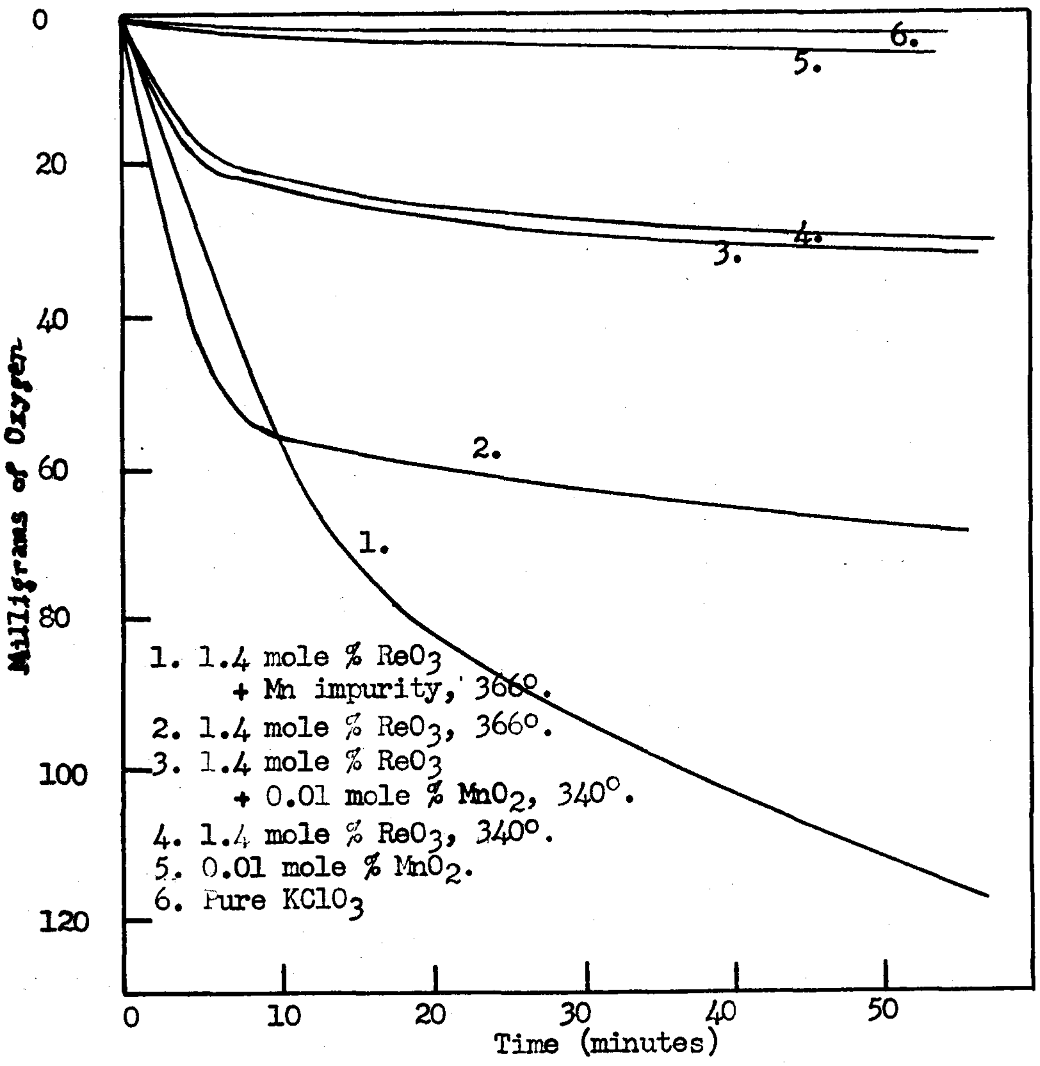

Figure 18. Decomposition of $KClO_3$ with ReO_3 Plus Trace of MnO_2

A mixture of potassium chlorate with a trace of manganese dioxide uniformly distributed in it was prepared by mixing a large batch and weighing out a sample from the batch. To accomplish this, 25.000 g. of 200 mesh $KClO_3$ and 0.0025 g. of 200 mesh MnO_2 were three times ground together, portion at a time, in an agate mortar with thorough shaking in a weighing bottle between grindings. Finally, the mixture was dried at 110° C., again ground, and again shaken in a weighing bottle. A 1.000 g. sample of this mixture contained 0.0001 grams of MnO_2, approximately 0.01 mole percent.

To a 1.0000 g. sample of the above mixture 0.0269 g. of ReO_3 (1.4 mole percent) was added by grinding in an agate mortar. The rate of decomposition of this mixture at 340° C. is shown as curve 3, Figure 18. Curve 4 is the decomposition of $KClO_3$ with 1.4 mole percent ReO_3 only. An increase in rate is noted for the sample with the trace of MnO_2.

Curve 5 is the decomposition at 340° C. of the $KClO_3$ containing 0.01 mole percent MnO_2. Curve 6 is the decomposition of pure $KClO_3$ at 340° C. Comparison of curves 5 and 6 shows the result of the catalytic activity of 0.01 mole percent MnO_2. This same activity is observed over and above that of the ReO_3 activity as can be seen by comparing 3 and 4. Thus, it is proved that in these cases MnO_2 does not promote the ReO_3 catalytic activity; instead, the total activity is the sum of the activities of both catalysts present. The experiment might more fully have answered the question concerning the abnormal decomposition shown in curve 1, Figure 18, had Mn metal been used in trace amount rather than MnO_2.

The result of the analysis of a residue from the decomposition of $KClO_3$ with ReO_3 plus a trace of manganese metal was included in previous data. Rhenium from the ReO_3 became perrhenate as shown in Figure 17, curve 7. Some of the trace of manganese ended up as permanganate as shown in Figure 12, curve 4. The small amount of insoluble manganese residue was not analyzed. Table XIII, run 5, includes the percentages of chloride, chlorate, and perchlorate in the residue from this run. Further studies on the effect of mixtures of rhenium and manganese catalysts on the decomposition of $KClO_3$ were not carried out.

OXYGEN^{18} AS TRACER IN THE CATALYTIC DECOMPOSITION OF $KClO_3$

Introduction

There is evidence that the catalytic action of manganese on the decomposition of potassium chlorate involves an alternate oxidation and reduction of the manganese. This evidence can be tested by enriching the oxygen of the catalyst with oxygen^{18} isotope. Oxygen liberated from chlorate decomposition with an enriched catalyst should contain oxygen^{18}.

Recently Forkushima et al (29) carried out a similar experiment. They enriched potassium chlorate with oxygen^{18} and decomposed it with $MnO_2 \cdot H_2O$ containing ordinary oxygen. Water was formed from successive portions of the liberated oxygen. The density of this water was less than the density of water prepared from oxygen liberated from $KClO_3$ without a catalyst. They concluded that some unstable compound is formed between $KClO_3$ and MnO_2, and that oxygen is liberated from this compound. They further concluded that only a limited portion of the catalyst is used in the reaction.

In the present experiment manganese dioxide was enriched with oxygen^{18}. Isotopic ratios of liberated oxygen were determined directly by use of a mass spectrograph.

Preparation of Oxygen^{18} Enriched Manganese Oxide

Water enriched with oxygen^{18} was obtained. It was thought to electrolyze the water and react the resulting oxygen with powdered manganese metal to prepare the MnO_2^{18}. Preliminary experiments, however, revealed that $MnO_{0.9}$ was the highest oxide obtainable by this method.

Tompkins (54) prepared manganese dioxide by reacting manganese chloride with potassium permanganate according to the following reaction:

$$Mn^{++} + 2MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

According to the mechanism of this reaction, as proposed by Tompkins, a part of the oxygen in the resulting MnO_2 comes from the water. Therefore, oxygen^{18} enriched manganese dioxide was prepared according to this reaction, by carrying out the precipitation in water enriched with oxygen^{18}.

Equivalent quantities of anhydrous $MnCl_2$ and $KMnO_4$ (0.7550 g. and 0.6322 g., respectively) were mixed and stirred into 3.0 ml. of water enriched with oxygen^{18}. A brown precipitate formed which was filtered and washed with two 1 ml. portions of H_2O^{18}. The wash water contained no permanganate.

The precipitate was dried in a desiccator connected to a vacuum pump for ½ hour. Then the evacuated desiccator was placed in an oven at 115° C. for 15 hours. At the end of this time the desiccator was again connected to a vacuum pump for $\frac{1}{2}$ hour.

Analysis by the bismuthate method showed 0.1000 g. of the oxide to contain 0.0569 g. of Mn. This corresponds to the formula, $MnO_{2.6}$, or nearly $MnO_2 \cdot H_2O$. That the oxide obtained was not exactly MnO_2 is not surprising, since Sakui et al (55) prepared manganese dioxide by eight methods and obtained eight formulas varying from $MnO_{1.28}$ to $MnO_{1.92}$.

Procedure

Collection of oxygen samples

A 0.2098 g. sample of the oxygen^{18} enriched catalyst was placed in the end of a 12 mm. x 10 cm. pyrex glass tube extending into a small electric furnace. The other end of the tube was connected by ground glass joints to a gas sampling tube, which in turn was connected to a high vacuum system. The gas sampling tube was a 12 mm. x 8 cm. pyrex glass tube with a high vacuum stopcock at each end, and with ground glass joints for connecting into the system. An acetone-dry ice trap was in the system to collect any moisture that might be liberated from the catalyst. A manometer, connected to the vacuum system, provided a measure of the pressure. The total volume of the vacuum system was approximately 60 ml.

The system was evacuated and the furnace was set at 360° C. No oxygen was liberated from the catalyst at this temperature as was noted by the manometer. The temperature was then raised to approximately 600° C. At this temperature the oxide decomposed enough to yield an oxygen pressure of 12.5 cm. The stopcocks on the sampling tube were closed and the sampling tube of oxygen was removed from the system to be analyzed (Sample 1, Table XV). A trace of frost formed in the acetone-dry ice trap while collecting the sample.

A mixture of 0.2450 g. $KClO_3$ and 0.2450 g. of enriched catalyst was placed in a reaction tube extending into another electric furnace. The reaction tube was connected by ground glass joints to a Y tube leading to two parallel gas sampling tubes. The other ends of the sampling bulbs were connected to a Y tube leading to a vacuum system with a manometer. The volume of the vacuum system was approximately 150 ml.

The system was evacuated through a stopcock to a vacuum pump line. Then one sampling tube was closed off and the other was left open. The furnace was set at 340° C. When the pressure of the system rose to 14.0 cm. Hg., the first sampling tube was closed off and the second was opened. With the reaction still in progress the pressure of the system was pumped down to a few mm. Hg. The vacuum pump was closed off until the pressure rose to 5 cm. Hg., and again was turned on to pump the pressure to a few mm. Hg. Finally the pump was again shut off and the reaction continued until no more oxygen could be liberated at 366° C. The oxygen pressure was 9.5 cm. in the system. The second sampling tube was then closed off. The sampling tubes of oxygen were then removed to be analyzed on the mass spectrograph. They furnished samples 2 and 3, Table XV. The collecting of samples 2 and 3 required approximately 10 minutes.

The residue was heated to 450° C. to be sure that all the $KClO_3$ was decomposed. Then the residue was heated to approximately 650° C. in an evacuated system containing another gas sampling tube. An oxygen pressure of 8 cm. developed from the decomposition of the residue manganese oxide. The sampling tube was shut off and the sample of oxygen was analyzed by the mass spectrograph (Sample 4, Table XV).

For determination of the normal O-32,O-34 ratio in oxygen, a sample of ordinary tank oxygen was analyzed (Sample 5, Table XV). For correcting for air leaks into the samples the oxygen-32, nitrogen ratio in air was determined by analysis of a sample of ordinary air (Sample 6, Table XV). In order to check for isotopic exchange between oxygen of the manganese oxide and surrounding oxygen, another experiment was carried out. Ordinary tank oxygen was placed over 0.200 g. of the oxygen^{18} enriched manganese oxide in a pyrex tube connected to a 60 ml. system for 1 hour at 340° C. A sampling tube of this oxygen was analyzed for oxygen^{18} (Sample 7, Table XV).

Fresh tank oxygen was then placed over this same sample of oxygen^{18} enriched manganese oxide for a much longer period of time, 15 hours, at 340° C. A sampling tube of this oxygen was analyzed for oxygen^{18} (Sample 8, Table XV).

Mass spectrograph analysis of samples

The sampling tubes, containing oxygen collected as shown above, were one by one connected to the high vacuum system of a mass spectrograph and analyzed for 0-32, 0-34 ratios according to a method described by Svec (56). Results of the analyses were automatically recorded as a series of voltage peaks versus mass numbers. The height of the peaks were functions of the mole fractions of any molecular weight species in the samples.

For these experiments interest was centered on mass numbers 32 and 34, corresponding to O^{16}-O^{16} and O^{16}-O^{18} molecules. Since the ratio of O^{16} to O^{18} in ordinary oxygen is only about 1 to 500 (37), O^{18}-O^{18} combinations are rare. Peaks for mass number 36, therefore, did not occur.

Comparisons of the amount of oxygen^{18} enrichment were made by comparing the $\frac{\text{O-32}}{\text{O-34}}$ ratio of each sample to that of ordinary oxygen. Since ratios were used for values, the units employed were not critical. Therefore, the ratios are ratios of millivolts readings from the calibrated peaks on the recorded chart paper.

Corrections were made for traces of air that leaked into the oxygen samples. In ordinary air the ratio $\frac{\text{O-32}}{\text{N-28} + \text{N-29} + \text{N-30}}$ is $\frac{1}{5.85}$. Assuming that any nitrogen present was proportional to the amount of air in the samples, one could solve for the O-32 in the air in a sample and subtract it from the O-32 voltage read from the chart. A similar correction for the O-34 can be applied. However, this correction proved to be practically negligible and was not applied in these results.

Results and Discussion

The results of these experiments are shown in Table XV. Sample 5 was ordinary tank oxygen, giving the normal ratio of $\frac{O\text{-}32}{O\text{-}34}$ to be 320. The factor times normal column was obtained by dividing the $\frac{O\text{-}32}{O\text{-}34}$ ratios of other samples into 320.

Sample 6 was a sample of air, confirming the correction factor $\frac{O\text{-}32}{N\text{-}28 + N\text{-}29 + N\text{-}30}$ to be 5.85.

Sample 1 contained 6.3 times the normal $\frac{O\text{-}34}{O\text{-}32}$ ratio, showing that the method of enriching the manganese oxide with O^{18} was successful.

Sample 2, the first of the oxygen liberated from the mixture of $KClO_3$ and manganese oxide, was enriched in $oxygen^{18}$ by a factor of 1.2 times normal. This showed that some of the oxygen liberated came from the catalyst.

Sample 3, the last part of the oxygen liberated during the catalytic decomposition of the $KClO_3$, was enriched in $oxygen^{18}$ by a factor of 1.4 times normal. Sample 4, obtained by decomposing the residue oxide, showed that the $oxygen^{18}$ content of the catalyst decreased during the reaction.

Sample 7 shows no $oxygen^{18}$ enrichment of the 60 ml. of tank oxygen that was in contact with 0.200 g. of the $oxygen^{18}$ enriched manganese oxide for 1 hour at 340° C. This is evidence that the $oxygen^{18}$ liberated during the 10 minutes of potassium chlorate decomposition was not just a result of isotopic exchange between oxygen liberated

Table XV

Results of Oxygen^{18} Tracer Experiment

Sample	0-32 (mv.)	0-34 (mv.)	N-28 N-29 N-30 (mv.)	$\frac{\text{0-32}}{\text{0-34}}$	Factor x Normal
1	3.187	0.063	0.0255	50.7	6.3
2	3.442	0.0131	0.0247	263	1.2
3	3.570	0.0153	0.0256	235	1.4
4	3.410	0.0527	0.0304	64.7	4.9
5*	3.654	0.0112	0.0318	320	1.00
6†	1.439	0.0057	8.43	---	---
7	3.722	0.0109	0.0387	341	0.97
8	3.129	0.0109	0.3963	224	1.4

*Tank oxygen.

†Sample of air.

from the chlorate and oxygen in the catalyst. However, sample 8 does show that some isotopic exchange had occurred after oxygen had been in contact with the catalyst for a 15 hour period at 340° C. Whether or not the water of hydration, probably present in the manganese oxide, was involved in this exchange was not determined.

These results prove that some of the manganese loses oxygen and then regains oxygen from the chlorate during catalytic decomposition of $KClO_3$. Not all the manganese atoms present, however, are involved in the catalysis when such large amounts of catalyst are present.

It appears that the manganese is undergoing a cyclic oxidation and reduction process. Once an oxygen^{18} atom is set free from the manganese, it is replaced by an oxygen^{16} from the chlorate. The next cycle involving this manganese atom, therefore, liberates ordinary oxygen. Oxygen^{18} enrichment of the liberated oxygen did not decrease during the decomposition; in fact, it increased slightly. This can be explained by the fact that only a part of the catalyst takes part in the reaction. As the reaction continues, the tiny particles of catalysts are broken into smaller particles, thus exposing more new manganese atoms at the surfaces. This accounts for the continued enrichment of the liberated oxygen.

The original catalyst was enriched with oxygen^{18} by a factor of 6.3 times normal. The residual oxide still contained 4.9 times the normal enrichment. This further indicates that only about 20% of the manganese was involved in the decomposition of 50 mole percent $KClO_3$.

These results are in agreement with the work of Forkushima et al (29).

DISCUSSION AND CONCLUSIONS

Practically no radioactivity was found in perchlorate formed during the decomposition of $KClO_3$ in the presence of KCl enriched with Cl^{36}. Neither was appreciable activity found in undecomposed chlorate in the residue. These facts prove that perchlorate is not formed by the addition of oxygen to chloride as was proposed by Glasner and Weidenfeld (23). Therefore, the mechanism of Otto and Fry (19,20), proposing that perchlorate formation is a reaction simultaneous with decomposition of chlorate to chloride, is still reasonable. The results also prove that no appreciable isotopic exchange occurs between chloride and perchlorate, or chloride and chlorate, under conditions of this experiment. These results and conclusions are in agreement with those of Vanden Bosch and Aten (25), who carried out a similar experiment using $NaClO_3$ in the presence of NaCl enriched with Cl^{34} and Cl^{38}.

During preliminary experiments on the preparation of the KCl^{36} for the above experiment, it was discovered that the presence of a small quantity of K_2CO_3 accelerates the decomposition of $KClO_3$ while hindering perchlorate formation. This finding is contrary to results reported by Fowler and Grant (8). The effect of carbonate on the decomposition of chlorate was not further explored.

Manganese chlorate was prepared and found to decompose explosively at 6° to 10° C. The instability of this compound led to a question of its involvement as a possible intermediate during the catalytic decomposition of $KClO_3$ with manganese catalysts. However, proof that the decomposition of manganese chlorate liberates chlorine oxide rather than oxygen discredits the possibility of this compound being an intermediate in the catalysis. It should be pointed out, however, that the temperature of the $KClO_3$ decompositions in this study and the decomposition temperature of the prepared $Mn(ClO_3)_2 \cdot 6H_2O$ are widely different. Whether or not temperature affects the type of manganese chlorate decomposition was not determined.

Results from the analysis of residues from the many potassium chlorate decompositions with the various catalysts reveal significant facts. For the manganese catalysts, regardless of the oxidation state of the manganese at the beginning of a reaction, at the end of the reaction the manganese existed in a mixture of states. Most of the manganese ended with an oxidation state of +3 to +4, but part of it ended in a portion extractable in water as permanganate. For the rhenium catalysts, regardless of the oxidation state of the rhenium at the beginning of a reaction, at the end of the reaction all of the rhenium existed only as a water soluble compound giving the perrhenate absorption spectrum. All the manganese catalysts exhibited a continued catalysis, whereas the rhenium catalysts gave catalytic action for a short time only.

The above facts can be explained by the theory that catalytic decomposition of $KClO_3$ occurs only during a change in oxidation state of the manganese or rhenium. Potassium perrhenate can be distilled at 1,370° C. without decomposition (58). Since perrhenate is so stable, catalysis stops with the rhenium catalysts as soon as the rhenium is oxidized to perrhenate. Since permanganate (or manganate) is relatively unstable, it decomposes as formed, and a cyclic oxidation and reduction of the active manganese atoms results so that a continued catalysis occurs.

Apparent activation energies for the decomposition of $KClO_3$ with the various catalysts were determined. For computing the activation energies it was assumed that the same reaction, decomposition of chlorate to chloride and oxygen, occurred during the first part of the reactions. Otto and Fry (20) report this reaction to be unimolecular. First order rate plots gave fairly straight lines over the first part of each reaction. Further, Arrhenius law plots, for four mixtures which were run at three or more temperatures, gave fairly straight lines. The apparent activation energy of 54 kcal. per mole for the decomposition of pure $KClO_3$ agrees with the value reported by

Glasner and Weidenfeld (22). These facts lend justification for the assumption that was made.

For the manganese catalysts, those with manganese in an intermediate oxidation state gave decompositions of $KClO_3$ with the lowest apparent activation energies. For the rhenium catalysts, also, the one with rhenium in an intermediate state (ReO_2) exhibited the lowest activation energy. The catalysis involved during the oxidation to perrhenate of the rhenium in all the various rhenium catalysts required only a low energy of activation.

The fact that Mn_3O_4, the catalyst exhibiting the lowest activation energy, was one of the poorer catalysts indicates that catalytic activity of a given catalyst depends upon the availability of manganese atoms for oxidation by the chlorate. The amount of surface and the condition of the surfaces of the catalyst particles are determining factors in the activity. The nature and structure of the compound also affects the activity of a catalyst. As was mentioned earlier, Sakui et al (55) prepared manganese dioxide by nine different methods for which analyses revealed nine slightly different manganese-oxygen ratios in the emperical formula. DeBroglie (59) reports that the structure of so-called manganese dioxide is quite complex and that the compounds of manganese oxides are extremely numerous and frequently inconsistent within themselves. Amiel, Brenet and Kodier (60,61) report that nine different samples of MnO_2 gave widely different rates of decomposition of H_2O_2.

If one assumes, however, that the same number of manganese atoms are available for catalysis for a given catalyst at more than one temperature, then activation energies serve as some measure of the activity of a catalyst. If it were possible to prepare catalysts with manganese in different oxidation states, but with similar surfaces and particle sizes, one might find that the catalyst giving a reaction with the lowest activation energy would be the best catalyst.

The fact that some fairly good catalysts for the decomposition of $KClO_3$ (Mn and $KMnO_4$) gave reactions with higher activation energies than that of pure $KClO_3$, itself, is not explained. The Arrhenius equation, written in exponential form,

$$k = A\ e^{-E/RT}$$

contains the constant, A, called the frequency factor. This constant is generally interpreted for higher order reactions as being equal to the frequency of collisions between reaction molecules (32). For reactions in which this factor is important, the activation energy derived from first order kinetics would not be reliable. Whether or not the frequency factor was significant during the first part of these reactions was not ascertained.

A conclusive check was carried out on the proposal that the catalytic activity of manganese on the decomposition of $KClO_3$ depends upon the oxidation and reduction of the manganese. Oxygen, liberated from a mixture of $KClO_3$ with MnO_2 enriched in oxygen^{18}, contained oxygen^{18}. Not all the manganese atoms were involved in the catalysis, however, as shown by the oxygen^{18} remaining in the catalyst after the reaction had occurred. These results agree with those of Forkushima et al (29) who reported results of a similar experiment while this work was in progress.

The results of the oxygen^{18} isotopic tracer experiment lead to the same conclusion reached from results of the analyses of residues; namely, that the active manganese atoms undergo alternate oxidation and reduction during the catalytic decomposition of $KClO_3$. That the change in oxidation state is necessary for the catalysis is proven by the fact that catalytic action with rhenium ceased when the rhenium was oxidized to stable perrhenate. Broughton and Wentworth (62) report that during the catalytic decomposition of H_2O_2 manganese also undergoes a series of alternate oxidations and reductions of the manganese.

SUMMARY

1. Little or no radioactivity was found in perchlorate formed during decomposition of $KClO_3$ with KCl enriched in Cl^{36}. Therefore, perchlorate is not formed by addition of oxygen to chloride during decomposition of $KClO_3$.

2. Manganese (II) chlorate ($Mn(ClO_3)_2.6H_2O$) was prepared and described. It decomposes to yield chlorine dioxide at 6° to 10° C.

3. The design, construction, and operation of an automatic recording balance is described. The balance will automatically plot changes in weight as a function of time with an uncertainty of ±0.2 milligrams over extended periods of time.

4. Decompositions of $KClO_3$ with a variety of manganese catalysts were carried out. Regardless of the oxidation state of the manganese at the beginning of the reaction, it ended in a mixture of states with most of the manganese in a +3 to +4 state and some of the manganese in a form extractable in water as permanganate.

5. Decomposition of $KClO_3$ with a variety of rhenium catalysts were carried out. Regardless of the oxidation state of the rhenium at the beginning of the reaction, it all ended up as perrhenate.

6. All manganese catalysts used exhibited a continued catalytic action, depending upon the temperature. All rhenium catalysts exhibited catalytic action only while being oxidized to perrhenate.

7. Apparent activation energies for decomposition of $KClO_3$ with the various catalysts were determined. The lowest activation energy for reactions with manganese catalysts was shown by Mn_3O_4. Rhenium dioxide gave the reaction with the lowest activation energy for rhenium catalysts. Decompositions of $KClO_3$ with rhenium catalysts take place with lower activation energies than decompositions with manganese catalysts.

8. $Oxygen^{18}$ appeared in the oxygen liberated when $KClO_3$ was decomposed by the aid of manganese oxide containing $oxygen^{18}$. Some $oxygen^{18}$ remained in the residue catalyst.

9. Results of these experiments lead to the conclusion that the catalytic decomposition of $KClO_3$ with manganese catalysts involves a succession of alternate oxidations and reductions of the active manganese atoms.

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