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The Kinetics Of The Acid Catalyzed Oxygen Exchange Between Chromium (vi) Oxyanions And Water

Scotty Yung Mak

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THE KINETICS OF THE ACID CATALYZED OXYGEN EXCHANGE 
BETWEEN CHROMIUM(VI) OXYANIONS AND WATER

by
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Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
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ABSTRACT

The mechanism of the oxygen exchange reaction between water and chromium(VI) oxyanions in acidic range has been investigated by the use of oxygen-18 enriched sodium chromate. The effect of pH, chromium(VI) concentration and chloride ion concentration on the rate of oxygen exchange was studied to obtain information about the mechanism of exchange.

Two paths of exchange are proposed for the exchange for pH between 4.5 and 7.0.

1. \( \text{Cr}_2\text{O}_7^{2-} + \text{HCrO}_4^- \overset{k_4}{\rightleftharpoons} \text{Cr}_3\text{O}_10^{2-} + \text{OH}^- \)

2. \( \text{HCr}_2\text{O}_7^- + \text{HCrO}_4^- \overset{k_5}{\rightleftharpoons} \text{Cr}_3\text{O}_10^{2-} + \text{H}_2\text{O} \)

A third path is involved above pH 7.0:

3. \( \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \overset{k_2}{\underset{k_{-3}}{\rightleftharpoons}} 2\text{HCrO}_4^- \)

A rate equation is developed for the calculation of the rate of oxygen exchange between water and Cr(VI) oxyanions:

\[ R = k_{-3} \left[ \text{HCrO}_4^- \right]^2 + k_4 \left[ \text{HCrO}_4^- \right]^3 + k_5 \left[ \text{H}^+ \right] \left[ \text{HCrO}_4^- \right]^3 \]

where \( R \) = rate of oxygen exchange.

The values of \( k_{-3}, k_4 \) and \( k_5 \) have been determined. They are:
\[ k_3 = 5.5 \text{ M}^{-1} \text{ sec}^{-1} \]
\[ k_4 = 13.6 \text{ M}^{-2} \text{ sec}^{-1} \]
\[ k_5 = 8.41 \times 10^7 \text{ M}^{-3} \text{ sec}^{-1} \]

For the chloride-catalyzed exchange reaction, a path involving the formation of a chloro-complex \( \text{CrO}_3\text{Cl}^- \) is proposed:

\[
\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[{k_{\text{Cl}^-}}]{k_{\text{Cl}^-}} \text{CrO}_3\text{Cl}^- + \text{Cr}_2\text{O}_4^{2-}
\]

And

\[ k_{\text{Cl}^-} = 48 \text{ M}^{-1} \text{ sec}^{-1} \]
ACKNOWLEDGMENTS

The author wishes to thank Dr. H.W. Baldwin for the suggestion of the problem, for his advice and encouragement during the entire investigation. He also wishes to express his gratitude to the Ontario Government for the Ontario Graduate Fellowship he received.

The author is especially grateful to his wife Julie for her assistance during the successful completion of the work.
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INTRODUCTION

Until 1923 there existed no direct, generally applicable method for measuring the rate of rapid chemical reactions in the liquid phase with half-times of less than 10 seconds. Hartridge and Roughton (1) in that year extended the observable time range about 10,000-fold by devising a method which could be used to follow reactions with half-lives ranging from 10 seconds (or more) down to 0.001 second. The principle of their method was that two reactant solutions are forced into a mixing chamber, and the mixed solution passes down an observation tube with a velocity \( u \) of several meters per second. A distance \( d \) from the mixing-chamber evidently corresponds to a time \( d/u \). The extent of reaction at various distances along the observation-tube (corresponding to various times) is found by measuring the optical density, electrical conductivity, or some other physical property of the solution. If there is no convenient physical method of following the reaction, chemical analysis may be used if the reaction can be quenched within an interval which is short compared to the time of the reaction. The flow velocity is found from the bore of the 1.
tube and the volume delivered over a measured time interval. With a flow velocity of ten meters per second, which is quite easy to produce, a distance of one cm. corresponds to 0.001 second, and reactions with half-times of this order can be observed.

In order for a flow apparatus to function satisfactorily, the time of complete mixing of reactants must be short in comparison with that taken by the chemical reaction, and laminar flow from the mixing chamber to the point of observation must be avoided. The first of these conditions is fulfilled by impelling the reactant solutions under pressure into a mixing chamber of suitable dimensions and design. A variety of types of mixing chambers have been used successfully; one type has four or more jets 0.5 to 1 mm. in diameter, arranged semi-tangentially, so the liquid acquires a rotating motion which accelerates mixing. Mixing is effectively complete within one or two milliseconds after leaving such a mixing chamber.

The second condition is satisfied only if there is homogeneous flow between the mixing chamber and point of observation. It is well known that the central parts of a fluid always tend to move faster than the average, whereas the peripheral parts move more slowly. Such deviations from mass flow are much more marked with stream-line than with turbulent flow.

The critical velocity for turbulent flow, \( u_c \), is given by Reynolds' formula:
\[ u_c = \frac{1000 \text{ (viscosity in poises)}}{(\text{density}) \cdot (\text{radius of tube in cm.})} \]  

All investigators have used rates of flow in excess of the critical velocity for turbulent flow, in order to reduce the errors in computing the rate constants which might result through deviation from mass flow.

For many years the flow method was used mainly by physiological and biological researchers; investigations include reactions of haemoglobin (3) and enzyme kinetics (4). Recently, however, the range of reactions studied has been extended tremendously. Table I illustrates the type of reactions that have been studied and the range of second order rate constants (k) that have been determined.

**TABLE I**

**REACTIONS STUDIED BY FLOW METHOD**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Method of detection</th>
<th>( k ) M(^{-1}) sec(^{-1} )</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Haemoglobin + O(_2)</td>
<td>photometry</td>
<td>(1.1 \times 10^7)</td>
<td>(3)</td>
</tr>
<tr>
<td>Haemoglobin + CO</td>
<td>photometry</td>
<td>(1.0 \times 10^6)</td>
<td>(4)</td>
</tr>
<tr>
<td>CO(_2) + OH(^-) \rightarrow HCO(_3^-)</td>
<td>thermal</td>
<td>(1.1 \times 10^3)</td>
<td>(5)</td>
</tr>
<tr>
<td>Cr(_2)O(_7^-) + H(_2)O</td>
<td>thermal</td>
<td>(5.0 \times 10^3)</td>
<td>(6)</td>
</tr>
<tr>
<td>I(_2) + HSO(_3^-)</td>
<td>photometry</td>
<td>(2.3 \times 10^9)</td>
<td>(9)</td>
</tr>
<tr>
<td>H(_2)O(_2) + Ce(_3^+)</td>
<td>photometry</td>
<td>(9.0 \times 10^5)</td>
<td>(8)</td>
</tr>
<tr>
<td>Fe(_3^+) + SCN(^-)</td>
<td>photometry</td>
<td>(1.3 \times 10^2)</td>
<td>(10)</td>
</tr>
</tbody>
</table>
The hydrolysis of dichromate by hydroxide ion was one of the earliest reactions examined by this method in the field of inorganic chemistry. The mechanism of the reaction will be discussed later.

Various species of Cr(VI) oxyanions exist at different pH's; hydrogenchromate ion, chromate ion and dichromate ion have been shown to be the main species above pH 1.5. Below this pH, various other species have also been postulated, for example, hydrogendichromate, chromic acid and polychromates. According to Sasaki (11) at pH about 8 to a pH of about 1.5, the hydrogenchromate ion and dichromate ion increase in concentration and become the predominant species as the pH decreases. The ratio of dichromate ion to hydrogenchromate ion increases as the pH decreases until at a pH of 5 where the ratio becomes constant. The following are the equilibrium equations and constants measured both potentiometrically and spectroscopically at 25°C and 3M ionic strength for chromium(VI) oxyanions (11).

\[
\begin{align*}
  H^+ + CrO_4^{2-} & \rightleftharpoons HCrO_4^- \\
  2HCrO_4^- & \rightleftharpoons Cr_2O_7^{2-} + H_2O
\end{align*}
\]

\[
\log K_1 = 5.89 \pm 0.02 \quad 5.91 \pm 0.01
\]

\[
\log K_2 = 2.20 \pm 0.02 \quad 2.18 \pm 0.08
\]

The hydrolysis of the dichromate ion in alkaline solution proceeds according to the stoichiometric equation:

\[
Cr_2O_7^{2-} + 20H^- \rightarrow 2CrO_4^{2-} + H_2O
\]
The reaction was found by La Mer and Read (7) to be first order with respect to dichromate ion and zero order with respect to hydroxide ion. The rate determining step therefore was assumed to be

\[ \text{a) } \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^- \]

followed by fast neutralization according to

\[ \text{b) } \text{HCrO}_4^- \rightarrow \text{CrO}_4^{2-} + \text{H}^+ \]

\[ \text{c) } \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

More recently, however, Lifshitz and Perlmutter-Hayman (12) found that the reaction between dichromate ion and several bases (including hydroxide ion) was first order in concentration of base and first order in concentration of dichromate ion, and this is more consistent with some earlier work of Saal (13) and Chance (14) and later confirmed by Wilkins (15). The recent measurements of the dichromate water reaction by a relaxation method (16) show that hydrolysis by water is much slower than base hydrolysis and this is further evidence that the observations of La Mer and Read are incorrect.

An \( S_{\text{N}2} \) mechanism was proposed by Lifshitz and Perlmutter-Hayman (12) for the general base (B) hydrolysis of dichromate.

1) \( \text{Cr}_2\text{O}_7^{2-} + \text{B} \xrightarrow{k_2^B} \text{BCrO}_3^- + \text{CrO}_4^{2-} \)

2) \( \text{BCrO}_3^- + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{HCrO}_4^- \)

3) \( \text{HCrO}_4^- + \text{B} \rightarrow \text{BH}^+ + \text{CrO}_4^{2-} \)  

\( \text{(For } \text{B} = \text{OH} \text{, step (2) is omitted) } \)
Table II shows the rate constants for the hydrolysis of dichromate by various bases.

**TABLE II**

**RATE CONSTANTS FOR HYDROLYSIS OF DICROMATE BY VARIOUS BASES**

<table>
<thead>
<tr>
<th>Base</th>
<th>$k_3$ M$^{-1}$ sec$^{-1}$</th>
<th>Method used</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>$4.6 \times 10^2$</td>
<td>continuous flow</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>$3.9 \times 10^2$</td>
<td>stopped flow</td>
<td>(15)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$9.3 \times 10^{-5}$</td>
<td>simple mixing</td>
<td>(18)</td>
</tr>
<tr>
<td></td>
<td>$4.6 \times 10^{-4}$</td>
<td>stopped flow</td>
<td>(15)</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$7.4 \times 10^2$</td>
<td>continuous flow</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>$8.6 \times 10^2$</td>
<td>stopped flow</td>
<td>(15)</td>
</tr>
<tr>
<td>C$_6$H$_5$O$^-$</td>
<td>$26.5 \pm 3.5$</td>
<td>continuous flow</td>
<td>(12)</td>
</tr>
<tr>
<td>C$_7$H$_9$N</td>
<td>0.5</td>
<td>stopped flow</td>
<td>(15)</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>$2.3 \times 10^3$</td>
<td>n.m.r.</td>
<td>(17)</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>10</td>
<td>continuous flow</td>
<td>(12)</td>
</tr>
<tr>
<td>H$_2$N-S-NH$_2$</td>
<td>17.2</td>
<td>u.v.</td>
<td>(19)</td>
</tr>
<tr>
<td>H$_2$N-C-NH$_2$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>u.v.</td>
<td>(19)</td>
</tr>
</tbody>
</table>
Nyholm, Figgis and Kidd (17) concluded that not only basic strength but other properties characteristic of good nucleophilic reagents play a role in the hydrolysis. They used polarizability as the additional criterion for nucleophilic character and obtained a reasonable correlation between the rate constants, basic strengths and polarizabilities of \( \text{OH}^- \), \( \text{CO}_3^{2-} \), \( \text{NH}_3 \) and \( \text{CrO}_4^{2-} \). Wilkins et al (15) found that the order of reactivity of the bases, \( \text{NH}_3 > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{C}_7\text{H}_5\text{N} > \text{H}_2\text{O} \), is consistent with their decreasing basicity if some allowance is made for electrostatic repulsion in the reaction with hydroxide ion and steric hindrance in the attack of 2, 6 lutidine.

As can be seen from the mechanisms suggested by La Mer and Read and by Lifshitz and Perlmutter-Hayman, the only possible path for oxygen exchange is through dimerization:

\[
1) \quad \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^- \\
2) \quad \text{Cr}_2\text{O}_7^{2-} + \text{OH}^- \rightleftharpoons \text{CrO}_4^{2-} + \text{HCrO}_4^- 
\]

The first mechanism is independent of hydroxide ion, while the second mechanism is first order with respect to hydroxide ion. Holoyer and Baldwin (18) have studied the system above pH 7 by the method of oxygen exchange and their results are in good agreement with those reported by Baloga and Earley (20).
Three processes are proposed by Holyer and Baldwin to account for oxygen exchange with the solvent:

a) \( \text{CrO}_4^{2-} + \text{H}_2\text{O} \xrightarrow{k_1} \text{CrO}_4^{2-} + \text{H}_2\text{O} \quad \text{with} \quad k_1' = 3 \times 10^{-7} \text{ sec}^{-1}, \text{ where} \quad k_1' = k_1[H_2O] \)

b) \( \text{HCrO}_4^- + \text{CrO}_4^{2-} \xrightarrow{k_2} \text{Cr}_2\text{O}_7^{2-} + \text{OH}^- \quad \text{with} \quad k_2 = 2.9 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} \)

\( k_2 = 2.3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1} \)

c) \( \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \xrightarrow{k_3} \text{2HCrO}_4^- \quad \text{with} \quad k_3' = 5 \times 10^{-3} \text{ sec}^{-1}, \text{ where} \quad k_3' = k_3[H_2O] \)

\( k_3 = 0.82 \text{ M}^{-1} \text{ sec}^{-1} \)

They have derived a rate law which follows the observed results closely. At high pH's process (a) is the most important for the exchange of oxygen. (Zero order in \([H^+]\) and first in \([\text{Cr(VI)}]\)). As the pH decreases, first the hydrogen chromate ion concentration and then the dichromate ion concentration becomes significant. This results in process (b), then process (c) becoming important.

According to the rate law derived by Holyer and Baldwin, the rate of exchange of oxygen, \( R \), is expressed as follows:

\[ R = k_1[H_2O] \left[ \text{CrO}_4^{2-} \right] + k_2 \left[ \text{CrO}_4^{2-} \right] \left[ \text{HCrO}_4^- \right] + k_3[H_2O] \left[ \text{Cr}_2\text{O}_7^{2-} \right] \]

The rate of exchange will be expected to approach a limiting value as the pH decreases since at lower pH's the concentration of \( \text{CrO}_4^{2-} \) is negligible and the ratio of concentrations of \( \text{HCrO}_4^- \) and \( \text{Cr}_2\text{O}_7^{2-} \) becomes constant.
No work has been published for the exchange of oxygen between Cr(VI) oxanions and water below pH 7. Initial experimental results and calculations showed that the above rate law does not hold if the pH is below 7. It is the aim of this research project to investigate the exchange reactions at lower pH's and to find out if other possible mechanism are involved.

Both Baloga and Earley and Holleyer and Baldwin used a standard mixing method; this was possible since exchange occurs relatively slowly above pH 7. However, in order to investigate the exchange reaction below pH 7, it was necessary to use a flow apparatus.
PART I

EXPERIMENTAL
A. Apparatus

1. Flow Machine - Fast Reactions

The apparatus used for mixing and sampling solutions is shown in Fig. 1 and Fig. 2. The solutions were forced from the reactant cylinders by pistons driven by a variable-speed motor. The rate of solution flow can be varied over a wide range and hence reaction time ranges from 0.03 second to 0.5 second can be obtained by varying the length of capillary tube and the rate of flow.

The mixing chamber was of conventional design (Fig. 2); the separate streams of solution entered the chamber tangentially and the combined stream leaving the capillary tube was then quenched with alkaline barium perchlorate. The reaction was therefore stopped as soon as the precipitate of barium chromate was formed which is very rapid. Thus the time between mixing and sampling is the time required for the solution to flow from the mixing chamber to the surface of the barium perchlorate solution.

The mixing chamber was made of lucite, and inlet tunnels were drilled 0.41 mm. in diameter. The bottom of
Figure 1
FLOW APPARATUS

Reservoirs
Pistons
Drive Shaft
Mixing Chamber
Capillary
To Motor
Figure 2

MIXING CHAMBER OF FLOW APPARATUS
the lucite block has a small depression and a separate lucite plate with six holes that can be fitted to the block. These six holes are intended to improve the efficiency of mixing. Finally a detachable brass metal block with a glass capillary can be attached to the bottom of the lucite plate which serves as an extension of the mixing chamber. Various lengths of capillary can be used as desired. Fig. 2 shows the detail of the mixing chamber.

2. Direct Mixing - Slow Reactions

For slow reactions \( t_{1/2} > 1 \) minute \( , \) equal volumes (200 ml.) of \( \text{Na}_2\text{CrO}_4^* \) and \( \text{H}_2\text{O} \) (at a desired pH achieved by addition of 0.1 M sodium hydroxide or 0.1 M of the appropriate acid) were mixed in a 600 ml. beaker equipped with a magnetic stirrer. Aliquots of solutions were taken out and quenched immediately. Since the reaction is very slow, the time required for sampling (2 seconds) is small when compared with the half-life.

3. High Vacuum System and Toepler Pump

A mechanical vacuum pump served as fore pump, and an attached mercury diffusion pump connected to the vacuum system produced a vacuum of better than \( 10^{-5} \) mm. Hg. Relative pressures were shown by a thermocouple gauge. The collection of oxygen gas samples was by the use of an automatic Toepler pump (21).
4. Mass Spectrometer

The mass spectrometer used has a double collector, and is similar to that described by Nier (22). It was found (18) that in the range of oxygen-18 enrichment employed, the plots of observed against calculated oxygen-18 to oxygen-16 ratio were linear. The mass spectrometer used did not give absolute values of the isotopic composition of the samples, but they gave the precise relative values required in this study.

5. pH meter

A Radiometer pH meter, type M4b was used for pH measurements in the kinetic runs. It was fitted with a Radiometer type G222B semi-micro glass electrode with low sodium ion correction, and a saturated calomel electrode. Standardization was made by buffer solutions made up to N.B.S. specifications. The two buffers used were supplied by the Beckman company, the two being respectively at a pH at 25°C of 6.86 ± 0.03 and 9.18 ± 0.01. The uncertainty in pH as measured by the pH meter is ± 0.02 pH units in the pH region 6.0 - 9.5 and is ± 0.05 pH units in the region 6.0 - 4.5.

B. Preparation of Chemicals

1. Sodium Chromate enriched in Oxygen-18

About 150 gms. of reagent grade sodium chromate was dissolved in water with oxygen-18 concentration about one
atom percent and the solution was refluxed for about ten hours. The solution was then placed in an evaporating dish in a desiccator. A mechanical pump was used to distil off the water, which was recovered from a dry ice-methanol trap. An infrared lamp was used to dry the sodium chromate further. The above procedure was repeated once more with two atom percent oxygen-18 water. After refluxing, the solution was filtered hot through a medium porosity sintered-glass funnel and was then placed in the desiccator for three days under an infrared lamp. 50 gm. lots of the enriched sodium chromate were powdered and dried at 250° by use of a vacuum system and then stored in a desiccator over anhydrous magnesium perchlorate.

2. Sodium Perchlorate

Reagent grade sodium perchlorate was used. It was dissolved in hot water and then filtered hot through a medium porosity sintered-glass funnel. The solution was allowed to cool and crystallize, and the water was then removed by ice cold filtration through a medium porosity sintered-glass funnel. The precipitate was dried overnight at 180°C in an evaporating dish and was then powdered and ready to be used.

3. Water

Distilled water from the laboratory was redistilled from potassium permanganate solution in a Pyrex glass system.
4. Oxygen-18 enriched water

The enriched water, containing approximately 1.73 atom percent oxygen-18, was supplied by the Weizmann Institute of Science, Israel.

5. Sodium Hydroxide

Standard sodium hydroxide solutions were prepared from a clear 40% solution of reagent grade sodium hydroxide pellets and standardized against potassium acid phthalate.

6. Hydrochloric Acid

Concentrated hydrochloric acid meeting A.C.S. reagent specifications was used without further purification in the preparation of standard hydrochloric acid. The acid was standardized against sodium carbonate and also against the standardized sodium hydroxide. No difference could be detected in the results obtained by the two procedures.

7. Perchloric Acid

70% perchloric acid meeting A.C.S. specifications was used without further purification. A solution of perchloric acid was standardized against standard sodium hydroxide prepared above, using phenolphthalein as indicator.

8. Acetic Acid

99.8% concentrated acetic acid meeting A.C.S. requirements was used without further purification. The acid was standardized against standard sodium hydroxide prepared above using phenolphthalein as indicator.
9. Sodium Acetate

Reagent grade anhydrous sodium acetate was dissolved in hot water and then filtered through a medium porosity sintered-glass funnel. The solution was allowed to cool and the solvent was removed by evaporation. The powder was then dried at 150°C for 20 hours.

10. Barium Perchlorate

Reagent grade anhydrous barium perchlorate was used without further purification.

C. General Experimental Procedures for Kinetic Runs

1. For Fast Reactions ($t_{1/2} < 1$ minute)

A weighed sample of enriched sodium chromate was dissolved in 100 ml. of normal water containing 2 mmole of sodium hydroxide in a 250 ml. volumetric flask; the solution was then made up to 250 ml. Standard acid solutions were made by diluting more concentrated standard solutions. 5 ml. each of acid solution and enriched sodium chromate solution were mixed in a 25 ml. beaker and the pH was determined in order that adjustment could be made for the bulk solutions before they were placed in the flow machine. The pH of each kinetic run was determined by taking the pH of a few ml. of the solution from the flow machine after each sampling and then averaging the pH's thus obtained. The quenching solution was prepared by dissolving a weighed amount of barium perchlorate in distilled water and enough sodium hydroxide was added to bring the pH above 10 after
quenching. Slightly less than the equivalent amount required for complete precipitation was used, as the precipitate obtained is easier to handle. About 20 ml. of quenching solution was placed in a 125 ml. Erlenmeyer flask, and after the flow machine was started, this solution was placed below the outlet of the mixing chamber. The characteristic yellow precipitate of barium chromate formed immediately. The precipitate thus obtained was allowed to digest for a few hours and then was filtered and washed with 25 ml. of distilled water several times. The filtration was done in a fine porosity crucible and the precipitate was dried in an oven at 120° for 24 hours. The time of reaction was calculated by the following formula:

\[ T = \frac{V}{V} \cdot t \]

where

\( T \) = time of reaction

\( V \) = volume of mixing chamber ml.

\( V \) = volume of solution (ml.) collected in t seconds.

A set of reaction times was therefore obtained by varying the speed of the motor of the flow machine. Samples of various reaction times together with a sample of starting material and a sample after equilibrium has been reached were analysed using the mass spectrometer for isotopic oxygen content.
2. For Slow Reaction ($t_{1/2} > 1$ minute)

The reaction was done in a 600 ml. beaker equipped with a magnetic stirrer. A Gralab electric stop clock was used for timing. Sampling was essentially the same as described above.

3. Isotopic Analysis of Enriched Chromate Samples

Barium chromate enriched in oxygen-18 was placed in a quartz tube which was connected to the closed high vacuum system through ground glass joints. The sample was heated strongly in a gas-oxygen flame for about five minutes, and the enriched oxygen evolved was transferred to a sample tube by means of an automatic Toepler pump. The gas samples of a series of runs were analysed by mass spectrometer for isotopic oxygen content.

D. Experiment to Determine the Efficiency of Mixing of the Flow Machine

The efficiency of mixing of the flow machine was tested in the following manner (1). Standard solutions of 0.050 M HCl and 0.055 M NaOH were prepared and the pH was found equal to 8 after equal volumes were mixed together. A few drops of phenolphthalein indicator was added to the hydrochloric acid solution. The flow machine was turned on and the solution that came out was carefully watched as it passed through the capillary tube. It was observed that in the first two seconds, the solution flashed a pink color and then colorless alternately. After two seconds, the pink
color stayed permanently, which signified that mixing was complete. In the subsequent kinetic runs the solution collected during the first five seconds was discarded in order to avoid any effects of incomplete mixing.
PART II

RESULTS AND CALCULATIONS
A. INITIAL TREATMENT OF DATA

1. Calculation of Exchange Rates

It was shown by MacKay (23) that the process of "simple isotopic exchange" in a homogeneous stable system can be described by a relatively simple exponential equation. The term "simple isotopic exchange" implies a system in which isotopic exchange is occurring between reactants uniformly distributed in the same phase and in which all conditions except for the distribution of isotopes between the reactants are constant during the course of the exchange reaction. Thus the only net change taking place in the system is a redistribution of isotopes towards isotopic equilibrium. The fact that the plots of $\log \left( \frac{N_t - N_\infty}{N_0 - N_\infty} \right)$ against time are linear indicates that these conditions are met.

Derivation of a MacKay type equation for the system studied here follows:

The net isotopic exchange occurring in the system is assumed to be

$$\text{Na}_2\text{CrO}_5^* + H_2O \rightleftharpoons H_2O^* + \text{Na}_2\text{CrO}_4$$

where $\text{Na}_2\text{CrO}_5^*$ and $H_2O^*$ are the species enriched in oxygen-18. Since $\text{Na}_2\text{CrO}_4$ contains four chemically equivalent oxygen atoms, the concentrations of $\text{Na}_2\text{CrO}_4$ and $\text{Na}_2\text{CrO}_5^*$ must by multiplied by four.
Let the concentrations at time $t$ be as follows:

$$\left[ H_2O \right] + \left[ H_2O^* \right] = a = \left[ 0 \right] + \left[ 0^* \right] \quad \text{in } H_2O + H_2O^*$$

$$4 \left[ Na_2CrO_4 \right] + 4 \left[ Na_2CrO_3O^* \right] = b = \left[ 0 \right] + \left[ 0^* \right] \quad \text{in } Na_2CrO_4 + Na_2CrO_3O^*$$

$$\left[ H_2O^* \right] = x, \left[ H_2O \right] = a - x$$

$$4 \left[ Na_2CrO_3O^* \right] = y = \left[ 0^* \right] \quad \text{in } Na_2CrO_3O^*$$

$$\left[ 0 \right] \quad \text{in } Na_2CrO_4 + Na_2CrO_3O^* = b - y + Ky$$

Let $R$ be the gross rate of exchange, i.e. the rate of exchange of all oxygen atoms regardless of isotopic nature. The assumption is made that there is no appreciable isotope effect.

The rate of change of $\left[ Na_2CrO_3O^* \right]$ is equal to its rate of consumption minus its rate of formation. The rate of consumption of $Na_2CrO_3O^*$ is given by the expression:

$$R = \frac{y}{a-x} \quad \text{where } \frac{y}{a-x} = \text{fraction of reactions with } O-16 \text{ of } Na_2CrO_3O^*$$

$$\frac{a-x}{4b} = \text{fraction of reactions with } H_2O^{16}$$

The rate of formation of $Na_2CrO_3O^*$ is given by:

$$R = \frac{x}{a-b-Ky} \quad \text{where } \frac{x}{a-b-Ky} = \text{fraction of reactions occurring with } H_2O^* \text{ and }$$

$$\frac{a}{b} = \text{fraction of reactions occurring with the oxygen-16 of } Na_2CrO_4.$$
The differential equation is given by:

\[
\frac{1}{4} \frac{dy}{dt} = R \cdot \frac{ky}{b} \cdot \frac{a-x}{a} - R \cdot \frac{b-ky}{b} \cdot \frac{x}{a}
\]

Therefore \( \frac{1}{4} \frac{dy}{dt} = \frac{R}{ab} (ky - bx) \) ..................(1)

Since the total number of oxygen-18 atoms in the system is constant

\[x + \frac{1}{4}y = x_\infty + \frac{1}{4}y_\infty \]  ...................(2)

where \(x_\infty\) and \(y_\infty\) are the oxygen-18 enrichments at infinite time, i.e. at isotopic equilibrium.

When equilibrium has been reached the isotopes are uniformly distributed, therefore:

\[\frac{ky_\infty}{b} = \frac{x_\infty}{a} \]  ...................(3)

from (2) and (3),

\[x = \frac{1}{4} \left( \frac{ay_\infty}{b} + y_\infty - y \right) \]  ...................(4)

Substituting (4) into (1), followed by separation of variables and simplification, the differential equation (5) is obtained

\[\frac{dy}{y - y_\infty} = \frac{R}{ab} \left( a + b \right) dt \]  ...................(5)

Integrating both sides of (5), and assuming \(R\) is a constant, independent of \(t\),

\[\ln (y - y_\infty) = \frac{R}{ab} \left( a + b \right) t + c \]  ...................(6)

where \(c\) is a constant of integration at \(t = 0, y = y_0\) and thus \(c = \ln (y_0 - y_\infty)\)
and \( \ln \left( \frac{y - y_\infty}{y_0 - y_\infty} \right) = \frac{R}{ab} \) \( a + b \) \( t \)

or \( \log \left( \frac{y - y_\infty}{y_0 - y_\infty} \right) = \frac{R}{ab \cdot 2.303} \) \( a + b \) \( t \)

Since the values of \( y \), \( y_0 \) and \( y_\infty \) are proportional to the \( N_t \), \( N_0 \) and \( N_\infty \) values obtained on the mass spectrometer, one obtains:

\( \log \left( \frac{N_t - N_\infty}{N_0 - N_\infty} \right) = \frac{R}{2.303} \) \( \frac{a + b}{ab} \) \( t \)

On rearranging and solving for \( R \),

\[
R = \frac{2.303 \cdot a \cdot b}{t} \cdot \left( \frac{N_t - N_\infty}{N_0 - N_\infty} \right) \]

Therefore, if \( \log \left( \frac{N_t - N_\infty}{N_0 - N_\infty} \right) \) is plotted against \( t \), a straight line is expected, and the rate \( R \) is given by

\[
R = -\text{ (slope of graph of semi-log plot )} \times 2.303 \left( \frac{ab}{a + b} \right) \]

Run No. A-10 is used for a sample calculation of the exchange rate \( R \). Table III is the data for this run and the plot is shown in Fig. 3.

From a least-squares fit, the slope of a semi-log plot of the above data = 1.15 sec\(^{-1} \), and

\( a = 55.33 \text{ gm-atom O liter} \)

\( b = 4 \times [\text{Cr(VI)}] = 0.20 \text{ gm-atom O liter} \)

whence \( R = 2.09 \text{ gm-atom O liter}\(^{-1} \text{ sec}^{-1} \). \)

In many of these plots the extent of reaction at zero time is not zero. This residual reaction may be due
to heat of solution produced on dissolving the enriched sodium chromate plus a net reaction leading to the equilibration of the species. The fact that the slopes of these plots are not affected by the zero time reaction was shown by choosing a slightly different $N_0$ value.

2. Calculation of Ionic Strength

The ionic strength of the exchange solutions was calculated by the equation of Lewis and Randall (24)

$$\mu = \frac{1}{2} \sum m_i z_i^2$$

where $\mu$ = ionic strength

$m_i$ = molality of ion i

$z_i$ = charge of ion i

The molal concentrations of each ion species in the solution was calculated, using equilibrium data for chromium(VI) species present in aqueous solution (25 to 28).
TABLE III

TYPICAL DATA FOR EXCHANGE RATE CALCULATION

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time of Exchange second</th>
<th>N_t</th>
<th>( \log \left( \frac{N_t - N_\infty}{N_0 - N_\infty} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-10-1</td>
<td>0.141</td>
<td>182.4</td>
<td>1.450</td>
</tr>
<tr>
<td>A-10-2</td>
<td>0.106</td>
<td>191.1</td>
<td>1.488</td>
</tr>
<tr>
<td>A-10-3</td>
<td>0.084</td>
<td>197.7</td>
<td>1.5152</td>
</tr>
<tr>
<td>A-10-4</td>
<td>0.059</td>
<td>204.3</td>
<td>1.5406</td>
</tr>
<tr>
<td>A-10-5</td>
<td>0.051</td>
<td>209.5</td>
<td>1.558</td>
</tr>
<tr>
<td>A-10-6</td>
<td>0</td>
<td>425.0</td>
<td>--</td>
</tr>
<tr>
<td>A-10-7</td>
<td>( \infty )</td>
<td>88.0</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 3  A KINETIC RUN SHOWING THE DEPENDENCE
ON TIME OF \( \log \left( \frac{N_t - N_{\infty}}{N_0 - N_{\infty}} \right) \)

RUN A-10
B. EXPERIMENTS TO DETERMINE THE RATE OF EXCHANGE OF OXYGEN

In Tables IV, V and VI are shown the rates of oxygen exchange obtained in experiments conducted by the methods outlined in Part I, Section C for a range of pH values in which the \[ \text{Cr(VI)} \] was constant at 0.2 M. The three tables represent the experimental results performed in three acid systems; perchloric acid, acetic acid-sodium acetate buffer solution and hydrochloric acid. In both the perchloric acid and hydrochloric acid systems, the ionic strength was kept at approximately 0.45 whereas in the acetic acid-acetate buffer, the ionic strength was 0.55. All experiments were performed at 25°C. The flow apparatus was used for all experiments between pH 4.6-7.0 and the standard mixing method was used for all experiments above pH 7.0.
### TABLE IV

EFFECT OF pH ON RATE OF OXYGEN EXCHANGE AT 25°C AND 

$[\text{Cr(VI)}] = 0.2 \text{ M}$

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>pH</th>
<th>$[\text{H}^+]$ M</th>
<th>R (gm-atom O l⁻¹sec⁻¹)</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-0</td>
<td>4.60</td>
<td>$2.51 \times 10^{-5}$</td>
<td>3.63</td>
<td>.560</td>
</tr>
<tr>
<td>A-1</td>
<td>4.80</td>
<td>$1.59 \times 10^{-5}$</td>
<td>3.40</td>
<td>.531</td>
</tr>
<tr>
<td>A-2</td>
<td>4.90</td>
<td>$1.26 \times 10^{-5}$</td>
<td>2.80</td>
<td>.450</td>
</tr>
<tr>
<td>A-3</td>
<td>5.00</td>
<td>$1.00 \times 10^{-5}$</td>
<td>2.41</td>
<td>.382</td>
</tr>
<tr>
<td>A-4</td>
<td>5.22</td>
<td>$6.03 \times 10^{-6}$</td>
<td>1.32</td>
<td>.120</td>
</tr>
<tr>
<td>A-5</td>
<td>5.35</td>
<td>$4.47 \times 10^{-6}$</td>
<td>1.08</td>
<td>.033</td>
</tr>
<tr>
<td>A-6</td>
<td>5.36</td>
<td>$4.37 \times 10^{-6}$</td>
<td>.935</td>
<td>- .029</td>
</tr>
<tr>
<td>A-7</td>
<td>5.40</td>
<td>$4.00 \times 10^{-6}$</td>
<td>.807</td>
<td>- .093</td>
</tr>
<tr>
<td>A-8</td>
<td>5.50</td>
<td>$3.16 \times 10^{-6}$</td>
<td>.795</td>
<td>- .100</td>
</tr>
<tr>
<td>A-9</td>
<td>5.60</td>
<td>$2.51 \times 10^{-6}$</td>
<td>.655</td>
<td>- .184</td>
</tr>
<tr>
<td>A-10</td>
<td>5.72</td>
<td>$1.91 \times 10^{-6}$</td>
<td>.522</td>
<td>- .282</td>
</tr>
<tr>
<td>A-11</td>
<td>5.80</td>
<td>$1.38 \times 10^{-6}$</td>
<td>.370</td>
<td>- .432</td>
</tr>
<tr>
<td>A-12</td>
<td>5.92</td>
<td>$1.20 \times 10^{-6}$</td>
<td>.285</td>
<td>- .545</td>
</tr>
<tr>
<td>A-13</td>
<td>6.00</td>
<td>$1.00 \times 10^{-6}$</td>
<td>.245</td>
<td>- .61</td>
</tr>
<tr>
<td>A-14</td>
<td>6.06</td>
<td>$8.71 \times 10^{-7}$</td>
<td>.224</td>
<td>- .650</td>
</tr>
<tr>
<td>A-15</td>
<td>6.30</td>
<td>$5.00 \times 10^{-7}$</td>
<td>.112</td>
<td>- .951</td>
</tr>
<tr>
<td>A-16</td>
<td>6.40</td>
<td>$4.00 \times 10^{-7}$</td>
<td>.097</td>
<td>-1.013</td>
</tr>
<tr>
<td>A-17</td>
<td>6.50</td>
<td>$3.16 \times 10^{-7}$</td>
<td>.0710</td>
<td>-1.15</td>
</tr>
<tr>
<td>A-18</td>
<td>6.70</td>
<td>$2.00 \times 10^{-7}$</td>
<td>.0400</td>
<td>-1.40</td>
</tr>
<tr>
<td>A-19</td>
<td>6.80</td>
<td>$1.32 \times 10^{-7}$</td>
<td>.0222</td>
<td>-1.658</td>
</tr>
<tr>
<td>A-20</td>
<td>7.20</td>
<td>$6.31 \times 10^{-8}$</td>
<td>.0050</td>
<td>-2.30</td>
</tr>
<tr>
<td>A-21</td>
<td>7.60</td>
<td>$2.51 \times 10^{-8}$</td>
<td>.00065</td>
<td>-3.18</td>
</tr>
<tr>
<td>A-22</td>
<td>8.02</td>
<td>$9.55 \times 10^{-9}$</td>
<td>.000073</td>
<td>-4.03</td>
</tr>
<tr>
<td>A-23</td>
<td>8.30</td>
<td>$5.01 \times 10^{-9}$</td>
<td>.000015</td>
<td>-4.60</td>
</tr>
</tbody>
</table>

Al-A19 Flow Apparatus

A20-A23 Standard Mixing

pH was fixed by addition of HClO₄ or NaOH

$\mu = 0.45$
TABLE V

EFFECT OF pH ON RATE OF OXYGEN EXCHANGE AT 25°C AND 
\([\text{Cr(VI)}] = 0.2 \text{ M}\)

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>pH</th>
<th>([H^+]) M</th>
<th>R (gm-atom O l^-1 sec^-1)</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>4.80</td>
<td>1.59x10^-5</td>
<td>3.23</td>
<td>.509</td>
</tr>
<tr>
<td>B-2</td>
<td>5.00</td>
<td>1.00x10^-5</td>
<td>2.46</td>
<td>.391</td>
</tr>
<tr>
<td>B-3</td>
<td>5.30</td>
<td>5.01x10^-6</td>
<td>1.08</td>
<td>.033</td>
</tr>
<tr>
<td>B-4</td>
<td>5.54</td>
<td>1.78x10^-6</td>
<td>.69</td>
<td>.16</td>
</tr>
<tr>
<td>B-5</td>
<td>5.63</td>
<td>1.48x10^-6</td>
<td>.66</td>
<td>.18</td>
</tr>
<tr>
<td>B-6</td>
<td>5.77</td>
<td>3.51x10^-7</td>
<td>.40</td>
<td>.40</td>
</tr>
<tr>
<td>B-7</td>
<td>5.86</td>
<td>7.94x10^-7</td>
<td>.37</td>
<td>.43</td>
</tr>
<tr>
<td>B-8</td>
<td>6.40</td>
<td>1.78x10^-7</td>
<td>.07</td>
<td>-1.15</td>
</tr>
</tbody>
</table>

All runs are in Flow Apparatus

pH was fixed by addition of HAc-NaAc buffer solution

\(\mu = 0.55\)
### TABLE VI

**EFFECT OF pH ON RATE OF OXYGEN EXCHANGE AT 25°C AND**

\( [\text{Cr(VI)}] = 0.2 \text{ M} \)

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>pH</th>
<th>( [\text{H}^+] ) M</th>
<th>( R ) (gm-atom O. 1^{-1}\text{sec}^{-1})</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>5.85</td>
<td>1.41x10^{-6}</td>
<td>.835</td>
<td>-.078</td>
</tr>
<tr>
<td>C-2</td>
<td>5.90</td>
<td>1.26x10^{-6}</td>
<td>.772</td>
<td>-.112</td>
</tr>
<tr>
<td>C-3</td>
<td>6.00</td>
<td>1.00x10^{-6}</td>
<td>.695</td>
<td>-.168</td>
</tr>
<tr>
<td>C-4</td>
<td>6.08</td>
<td>8.52x10^{-7}</td>
<td>.535</td>
<td>-.272</td>
</tr>
<tr>
<td>C-5</td>
<td>6.14</td>
<td>7.24x10^{-7}</td>
<td>.500</td>
<td>-.300</td>
</tr>
<tr>
<td>C-6</td>
<td>6.23</td>
<td>5.91x10^{-7}</td>
<td>.415</td>
<td>-.382</td>
</tr>
<tr>
<td>C-7</td>
<td>6.50</td>
<td>3.16x10^{-7}</td>
<td>.225</td>
<td>-.648</td>
</tr>
<tr>
<td>C-8</td>
<td>6.60</td>
<td>2.51x10^{-7}</td>
<td>.168</td>
<td>-.775</td>
</tr>
<tr>
<td>C-9</td>
<td>6.80</td>
<td>1.59x10^{-7}</td>
<td>.112</td>
<td>-.951</td>
</tr>
</tbody>
</table>

*All runs are in Flow Apparatus*

*pH was fixed by addition of HCl*

\( \mu = 0.45 \)
Tables VII and VIII show the rates of exchange of oxygen obtained in similar experiments in which the concentration of Cr(VI) was kept constant at 0.1 M, and the acids used are perchloric acid and hydrochloric acid.

**TABLE VII**

**EFFECT OF pH ON RATE OF OXYGEN EXCHANGE AT 25°C AND**

\[
[\text{Cr(VI)}] = 0.1 \text{ M}
\]

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>pH</th>
<th>([H^+]) M</th>
<th>(R) (gm-atom (1)-l-sec-1)</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>7.00</td>
<td>1.00x10^-7</td>
<td>0.0080</td>
<td>-2.097</td>
</tr>
<tr>
<td>D-2</td>
<td>7.05</td>
<td>8.91x10^-8</td>
<td>0.00213</td>
<td>-2.671</td>
</tr>
<tr>
<td>D-3</td>
<td>7.20</td>
<td>6.31x10^-8</td>
<td>0.00089</td>
<td>-3.052</td>
</tr>
<tr>
<td>D-4</td>
<td>7.35</td>
<td>4.47x10^-8</td>
<td>0.00039</td>
<td>-3.409</td>
</tr>
<tr>
<td>D-5</td>
<td>7.45</td>
<td>3.55x10^-8</td>
<td>0.00025</td>
<td>-3.598</td>
</tr>
<tr>
<td>D-6</td>
<td>7.65</td>
<td>2.24x10^-8</td>
<td>0.000076</td>
<td>-4.122</td>
</tr>
<tr>
<td>D-7</td>
<td>7.95</td>
<td>1.12x10^-8</td>
<td>0.000025</td>
<td>-4.598</td>
</tr>
<tr>
<td>D-8</td>
<td>8.08</td>
<td>8.32x10^-9</td>
<td>0.000012</td>
<td>-4.908</td>
</tr>
<tr>
<td>D-9</td>
<td>8.35</td>
<td>4.47x10^-9</td>
<td>0.000004</td>
<td>-5.402</td>
</tr>
</tbody>
</table>

Standard Mixing Method

pH was fixed by addition of HClO₄

\[\mu = 0.15\]


**TABLE VIII**

**EFFECT OF pH ON RATE OF OXYGEN EXCHANGE AT 25°C AND**

\[
\text{[Cr(VI)]} = 0.1 \text{ M}
\]

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>pH</th>
<th>([H^+] \text{ M})</th>
<th>(R \text{ (gm-atom O l}^{-1}\text{sec}^{-1}))</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>7.00</td>
<td>1.00 \times 10^{-7}</td>
<td>.00201</td>
<td>-2.70</td>
</tr>
<tr>
<td>E-2</td>
<td>7.20</td>
<td>6.31 \times 10^{-8}</td>
<td>.00092</td>
<td>-3.04</td>
</tr>
<tr>
<td>E-3</td>
<td>7.32</td>
<td>4.79 \times 10^{-8}</td>
<td>.00046</td>
<td>-3.34</td>
</tr>
<tr>
<td>E-4</td>
<td>7.41</td>
<td>3.89 \times 10^{-8}</td>
<td>.00027</td>
<td>-3.57</td>
</tr>
<tr>
<td>E-5</td>
<td>7.63</td>
<td>2.95 \times 10^{-8}</td>
<td>.000075</td>
<td>-4.12</td>
</tr>
</tbody>
</table>

**Standard Mixing Method**

pH was fixed by addition of HCl

\(\mu = 0.15\)
The dependence of the rate of oxygen exchange on the concentration of Cr(VI) is shown in Table IX. The pH was kept constant at 7.50 (perchloric acid system), 6.00 and 5.00 (acetic acid-acetate buffer system). The latter two series of runs were conducted in a buffer system in order to minimize fluctuation in pH, since these experiments were performed in the flow apparatus.

**TABLE IXa**

**EFFECT OF Cr(VI) CONCENTRATION ON THE RATE OF OXYGEN EXCHANGE AT 25°C**

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>[Cr(VI)] M</th>
<th>pH</th>
<th>LOG [Cr(VI)]</th>
<th>R (gm-atom O l⁻¹ sec⁻¹)</th>
<th>LOG R</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>0.100</td>
<td>7.45</td>
<td>-1.000</td>
<td>.00200</td>
<td>-2.699</td>
</tr>
<tr>
<td>F-2</td>
<td>0.080</td>
<td>7.50</td>
<td>-1.097</td>
<td>.00117</td>
<td>-2.931</td>
</tr>
<tr>
<td>F-3</td>
<td>0.060</td>
<td>7.51</td>
<td>-1.222</td>
<td>.000692</td>
<td>-3.160</td>
</tr>
<tr>
<td>F-4</td>
<td>0.040</td>
<td>7.50</td>
<td>-1.398</td>
<td>.000301</td>
<td>-3.522</td>
</tr>
<tr>
<td>F-5</td>
<td>0.020</td>
<td>7.48</td>
<td>-1.699</td>
<td>.0000738</td>
<td>-4.132</td>
</tr>
</tbody>
</table>

pH = 7.50 Standard Mixing Method

pH was fixed by addition of HClO₄

\( \mu = 0.45 \)
### TABLE IXb

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>[Cr(VI)] M</th>
<th>pH</th>
<th>( \log [H\text{CrO}_4^-] )</th>
<th>( R ) (gm-atom 0 l(^{-1})sec(^{-1}))</th>
<th>( \log R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-1</td>
<td>0.20</td>
<td>5.90</td>
<td>-1.506</td>
<td>3.21</td>
<td>-0.493</td>
</tr>
<tr>
<td>G-2</td>
<td>0.16</td>
<td>5.90</td>
<td>-1.564</td>
<td>1.19</td>
<td>-0.719</td>
</tr>
<tr>
<td>G-3</td>
<td>0.12</td>
<td>5.97</td>
<td>-1.642</td>
<td>0.95</td>
<td>-1.022</td>
</tr>
<tr>
<td>G-4</td>
<td>0.08</td>
<td>6.00</td>
<td>-1.752</td>
<td>0.44</td>
<td>-1.356</td>
</tr>
<tr>
<td>G-5</td>
<td>0.04</td>
<td>6.00</td>
<td>-1.921</td>
<td>0.05</td>
<td>-1.800</td>
</tr>
</tbody>
</table>

**pH = 6.00**, Flow Apparatus

pH was fixed by addition of HAc-NaAc

\( \mu = 0.45 \)

### TABLE IXc

<table>
<thead>
<tr>
<th>SERIES NO.</th>
<th>[Cr(VI)] M</th>
<th>pH</th>
<th>( \log [H\text{CrO}_4^-] )</th>
<th>( R ) (gm-atom 0 l(^{-1})sec(^{-1}))</th>
<th>( \log R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>0.20</td>
<td>5.00</td>
<td>-1.467</td>
<td>2.46</td>
<td>0.391</td>
</tr>
<tr>
<td>H-2</td>
<td>0.15</td>
<td>5.04</td>
<td>-1.536</td>
<td>1.34</td>
<td>0.127</td>
</tr>
<tr>
<td>H-3</td>
<td>0.12</td>
<td>5.05</td>
<td>-1.590</td>
<td>0.89</td>
<td>-0.051</td>
</tr>
<tr>
<td>H-4</td>
<td>0.10</td>
<td>5.04</td>
<td>-1.634</td>
<td>0.68</td>
<td>-0.165</td>
</tr>
<tr>
<td>H-5</td>
<td>0.08</td>
<td>5.02</td>
<td>-1.690</td>
<td>0.48</td>
<td>-0.317</td>
</tr>
<tr>
<td>H-6</td>
<td>0.05</td>
<td>4.95</td>
<td>-1.810</td>
<td>0.25</td>
<td>-0.590</td>
</tr>
</tbody>
</table>

**pH = 5.00**, Flow Apparatus

pH was fixed by addition of HAc-NaAc buffer

\( \mu = 0.45 \)
Plots of log R against -log[H⁺] at [Cr(VI)] = 0.2 M and 0.1 M are shown in Figs. 4 and 5. The various acid systems used are indicated in the graphs. A consistent trend is observed for all experimental data except at pH 4.6. This inconsistency may be due to the limit of the flow machine since an experiment performed at pH = 4.4 gave all $N_t = N_\infty$ which indicates that the reaction is too fast for the flow machine.

Figs. 6, 7 and 8 show the dependence of rate of oxygen exchange on $[\text{HCrO}_4^-]$ (graphs IV, V) and $[\text{Cr(VI)}]$ (graph VI) at pH 5.00, 6.00 and 7.45 respectively.

The calculation of concentration of $\text{HCrO}_4^-$, $\text{Cr}_2\text{O}_7^{2-}$ and $\text{CrO}_4^{2-}$ is now discussed.

The equilibrium equations are, according to Sasaki,

$$H^+ + \text{CrO}_4^{2-} \rightleftharpoons \text{HCrO}_4^-$$

$$2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + H_2O$$

and hence

$$K_1 = \frac{[\text{HCrO}_4^-]}{[H^+] [\text{CrO}_4^{2-}]}$$

$$K_2 = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{HCrO}_4^-]^2}$$
Figure 4. EFFECT OF pH ON RATE OF OXYGEN EXCHANGE
Figure 5 EFFECT OF pH ON RATE OF OXYGEN EXCHANGE
Figure 6  EFFECT OF $[\text{HCrO}_4^-]$ ON RATE OF OXYGEN EXCHANGE AT pH 7.50
Figure 7  EFFECT OF $[\text{HCrO}_4^-]$ ON RATE OF OXYGEN EXCHANGE AT pH 6.00

$log R$ vs. $log [\text{HCrO}_4^-]$ for Series G
Figure 8 EFFECT OF $[\text{HC}_2\text{O}_4^-]$ ON RATE OF OXYGEN EXCHANGE AT pH 5.00
Table X shows the values of $K_1$ and $K_2$ reported by several investigators at various ionic strengths and Fig. 9 shows the variation of $K_1$ and $K_2$ with ionic strength. The appropriate values of $K_1$ and $K_2$ for calculation of the concentrations of various species were taken from Fig. 9.

<table>
<thead>
<tr>
<th>REFERENCE</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>IONIC STRENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>$7.94 \times 10^5$</td>
<td>159</td>
<td>3.0</td>
</tr>
<tr>
<td>25</td>
<td>$1.35 \times 10^6$</td>
<td>--</td>
<td>0.11</td>
</tr>
<tr>
<td>26</td>
<td>$3.16 \times 10^6$</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td>--</td>
<td>98.0</td>
<td>1.0</td>
</tr>
<tr>
<td>28</td>
<td>--</td>
<td>33.0</td>
<td>0</td>
</tr>
<tr>
<td>Values used in present study</td>
<td>$1.3 \times 10^6$</td>
<td>70.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 9  VARIATION OF $K_1$ AND $K_2$ WITH IONIC STRENGTH
From the data tabulated in Part B, it can be seen that a decrease in pH increases the rate of exchange; also an increase in concentration of Cr(VI) increases the rate of exchange. Therefore, the rate of oxygen exchange should follow the rate law: \( R = k_i \left[ H^+ \right]^{n_i} \left[ \text{Cr(VI)} \right]^{m_i} \) where \( k_i \) is the rate constant for the ith oxygen exchange path, \( n_i \) is the order of \( [H^+] \) dependence for the ith oxygen exchange path, and \( m_i \) is the order of \( [\text{Cr(VI)}] \) dependence for the ith oxygen exchange path.

As can be seen from Fig. 4 and Fig. 5, the \([H^+]\) dependence on the rate of oxygen exchange can be divided into three sections, they are as follows:

pH 4.6-5.4 ; pH 5.4-7.0 and pH 7.0-8.4 .

In the perchloric acid system (A series) for pH 4.6-5.4 , the plot of log \( R \) vs-log[H+] at constant Cr(VI) concentration (0.2 M) gives a slope of 0.82; a slope of 1.1 was obtained for pH 5.4-7.0 . For pH 7.0-8.4 the slope was found to be 2.2 . A least-squares fit was employed to obtain the above slopes. For a lower concentration of Cr(VI) (0.1 M), an almost identical slope (2.3) was obtained from both perchloric acid and hydrochloric systems (series D & E) in the pH region 7.0-8.4 .

Below pH 5.5 in the hydrochloric acid system, the pH obtained after each sampling was not very steady. (Error = ± 0.2 pH units). In order to minimize error in the pH reading, a buffer system was employed. The buffer
solution chosen in the experiments was acetic acid-sodium acetate and the pH fluctuation was reduced to ±0.05 pH units. The rate of oxygen exchange agrees very well with that of the perchloric system (A series).

The rate of oxygen exchange was found to be much faster in hydrochloric acid than in perchloric acid (pH 5.4-7.0 region; \([\text{Cr(VI)}] = 0.2 \text{ M}\)). However, the slopes of the plot of log R vs-log \(H^+\) are the same in both media. An attempt to explain this unexpected result will be discussed later.

From least-squares fits of Figs. 6, 7 and 8, the following dependence of rate of oxygen exchange on \([\text{HCrO}_4^-]\) and \([\text{Cr(VI)}]\) was obtained. At pH 4.6-5.4 an order of 3.3 with respect to \([\text{HCrO}_4^-]\) was observed and at pH 5.4-7.0 an order of 2.9 with respect to \([\text{HCrO}_4^-]\) was found. For the pH region of 7.0-8.4, the rate of oxygen exchange shows approximately second order dependence with respect to \([\text{Cr(VI)}]\).

From the data calculated in this section the following conclusions can be drawn:

\[
\begin{align*}
\text{pH 4.5-5.4} & \quad R \propto [H^+]^{0.82} [\text{HCrO}_4^-]^{3.14} \\
\text{pH 5.4-7.0} & \quad R \propto [H^+]^{1.11} [\text{HCrO}_4^-]^{2.89} \\
\text{pH 7.0-8.4} & \quad R \propto [H^+]^{2.09} [\text{Cr(VI)}]^{2.10}
\end{align*}
\]
D. EFFECT OF IONIC STRENGTH

A comparison of the rate of oxygen exchange between series A (Perchloric acid system, \( \mu = 0.45 \text{ M} \)) and series B (acetic acid-sodium acetate buffer \( \mu = 0.55 \text{ M} \)) shows no difference in the results obtained. The total ionic strength in series A was obtained from the sum of ionic strengths of Cr(VI) species and sodium perchlorate, whereas the total ionic strength in series B was obtained from the sum of Cr(VI) species and sodium acetate. It can therefore be concluded that ionic strength does not have any significant effect on the rate of oxygen exchange within the concentration range employed in this study.

E. ERRORS

Percentage error in \( R \), (the rate of exchange of oxygen-18 between sodium chromate and water)

\[
R = -2.303 \left( \log \frac{N_e - N_t}{N_e - N_0} \right) \left( \frac{ab}{a + b} \right) = -2.303 \text{ slope of semi-log plot} \cdot \frac{ab}{a + b}
\]

One of the sources of error in obtaining \( R \) is the uncertainty in the slope of the plot of \( \log \frac{N_t - N_\infty}{N_0 - N_\infty} \) against \( t \).

It was shown (16) that in most reactions the standard percentage error of the slope was approximately 2%. In several exchanges, the standard percentage error was much
higher, especially in the cases where the number of samples obtained for a particular exchange reaction was less than four.

The percentage error in \( \frac{ab}{a + b} \) is insignificant; being about 0.3% when compared to the standard percent error in the slope. Therefore, the standard percentage error in R is usually about 2%. 
PART III

DISCUSSION
DISCUSSION

As was mentioned in the introduction to this thesis, the rate law derived by Holyer and Baldwin (18) from their studies on oxygen exchange between Cr(VI) oxyanions and solvent water at pH above 7 does not adequately describe the rapid exchange below pH 7. Their rate law:

$$R = k_1[H_2O][CrO_4^{2-}] + k_2[CrO_4^{2-}][HCrO_4^{2-}] + k_3[H_2O][Cr_2O_7^{2-}]$$

predicts a limiting rate will be reached below pH 6-6.5, where the dimerization equilibrium predicts an almost constant ratio of $$[Cr_2O_7^{2-}]$$ to $$[HCrO_4^-]$$ and vanishingly small concentrations of $$CrO_4^{2-}$$. The object of this research project is to obtain further data on oxygen exchange below pH 8 to permit expansion of the rate law, so further inferences may be drawn regarding the mechanism or mechanisms by which exchange is effected. Such information is obtained from studying the dependence of rate of exchange of oxygen on pH and Cr(VI) concentration. A summary of the experimental results dealing with the effect of $$[H^+]$$ and $$[Cr(VI)]$$ on the rate of oxygen exchange is given at the end of Part II, section C and is repeated here:

51.
\[ \text{pH 4.6 - 5.4} \quad R \propto \text{constant} \left[ H^+ \right]^{0.82} \left[ \text{HCrO}_4^- \right]^{3.14} \]
\[ \text{pH 5.4 - 7.0} \quad R \propto \text{constant} \left[ H^+ \right]^{1.11} \left[ \text{HCrO}_4^- \right]^{2.89} \]
\[ \text{pH 7.0 - 8.4} \quad R \propto \text{constant} \left[ H^+ \right]^{2.09} \left[ \text{Cr(VI)} \right]^{2.10} \]

From the equilibria
\[ K_1 = \frac{\left[ \text{HCrO}_4^- \right]}{\left[ H^+ \right] \left[ \text{CrO}_4^{2-} \right]} \]
\[ K_2 = \frac{\left[ \text{Cr}_2\text{O}_7^{2-} \right]}{\left[ \text{HCrO}_4^- \right]^2} \]

and the following material balance equation:
\[ \left[ \text{CrO}_4^{2-} \right] + \left[ \text{HCrO}_4^- \right] + 2 \left[ \text{CrO}_7^{2-} \right] = \left[ \text{Cr(VI)} \right] \]

it can be shown that for
\[ \text{pH} > 7.0 \quad \left[ \text{HCrO}_4^- \right] \propto \left[ H^+ \right] \left[ \text{Cr(VI)} \right] \quad \text{and for} \]
\[ \text{pH} < 5.4 \quad \left[ \text{HCrO}_4^- \right] \propto \left[ \text{Cr(VI)} \right] \]

However, such a simple relationship does not exist within the region of pH 5.4-7.0, so while it is reasonable to ascribe principal importance to a path \( \left[ H^+ \right] \left[ \text{HCrO}_4^- \right]^3 \) in the lowest pH region, it is reasonable to assume that an acid independent path \( \left[ \text{HCrO}_4^- \right]^3 \) may be important in the intermediate region and in the higher pH (7.0-8.4) region.

The results obtained for pH between 7.00-8.40 agree very well with the data reported by Baloga and Earley (20) and Holyer and Baldwin (18); both groups showed that within this pH range the rate of oxygen exchange displays second order dependence on the concentration of Cr(VI) and second
order dependence on $[H^+]$ (18). In the systems HClO$_4$ and 
HAc–NaAc buffer, the rates of exchange as a function of 
pH agree very well, but exchange is much faster in the 
HCl system.

According to Holleyer and Baldwin (18) at pH between 
7.0–12.0, the following mechanisms are responsible for the 
exchange process

(i) \[ \text{CrO}_4^{2-} + H_2O \xrightarrow{k_1/k_{-1}} \text{CrO}_4^{2-} + H_2O \]

(ii) \[ \text{HCrO}_4^- + \text{CrO}_4^{2-} \xrightarrow{k_2/k_{-2}} \text{Cr}_2\text{O}_7^{2-} + \text{OH}^- \]

(iii) \[ \text{Cr}_2\text{O}_7^{2-} + H_2O \xrightarrow{k_3/k_{-3}} 2\text{HCrO}_4^- \]

and at pH between 7.0–8.4, mechanism (iii) is predominant. 
However, from initial calculations using

\[ R = k_{-3} [\text{HCrO}_4^-]^2 \]

where \( R \) = rate of exchange

\( k_{-3} \) = rate constant for this process (18).

this mechanism alone cannot account for the fast rate 
observed in the present study.

Since an approximate third order dependence of $[\text{HCrO}_4^-]$ 
was found below pH 7.00, it therefore seems possible that a 
trichromate ion path may be involved. The fact that the 
dependence on $[\text{HCrO}_4^-]$ is slightly greater than two for 
pH 7.00–8.40 suggests that such a path may make some con-
tribution in this pH range, and account for the fast observed 
rate of exchange. The existence of the trichromate ion has
been shown by Martens and Carpeni (29). They expressed the equilibrium for polymerization as

\[ 3 \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightleftharpoons 2\text{Cr}_3\text{O}_{10}^{2-} + \text{H}_2\text{O} \]

and obtained a pK value -0.76. Therefore

\[ \frac{[\text{Cr}_3\text{O}_{10}^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]^3} \frac{[\text{H}_2\text{O}]}{[\text{H}^+]^2} = 0.17 \]

For Cr(VI) = 0.2 M,

at pH = 6 , \[ [\text{Cr}_3\text{O}_{10}^{2-}] = 1.0 \times 10^{-8} \text{ M} \]

at pH = 5 , \[ [\text{Cr}_3\text{O}_{10}^{2-}] = 1.0 \times 10^{-7} \text{ M} \]

At pH 7.0-8.4, if we assume two paths are important, path (iii) and

(iv) \[ \text{HCrO}_4^- + \text{Cr}_2\text{O}_7^{2-} \rightleftharpoons \text{Cr}_3\text{O}_{10}^{2-} + \text{OH}^- \]

then \( R = k_3[\text{HCrO}_4^-]^2 + k_4[\text{HCrO}_4^-][\text{Cr}_2\text{O}_7^{2-}] \)

and since \[ [\text{Cr}_2\text{O}_7^{2-}] = K_2 [\text{HCrO}_4^-]^2 \]

where \( K_2 \) is the equilibrium constant, therefore

\[ R = k_{-3}[\text{HCrO}_4^-]^2 + k_4K_2[\text{HCrO}_4^-]^3 \] and

\[ \frac{R}{[\text{HCrO}_4^-]^2} = k_3 + k_4K_2[\text{HCrO}_4^-] \] . When \( \frac{R}{[\text{HCrO}_4^-]^2} \) is plotted against \([\text{HCrO}_4^-]\), one obtains \( k_4K_2 \) as the slope and \( k_3 \) as the intercept. From the method of least-squares,
it was found that
\[ k_{-3} = 5.5 \, \text{M}^{-1} \, \text{sec}^{-1} \]
\[ k_4 k_2 = 950 \, \text{M}^{-2} \, \text{sec}^{-1} \quad \text{(Fig. 10, Table XI)} \]
\[ k_4 = 13.6 \, \text{M}^{-2} \, \text{sec}^{-1} \]

An alternate method was used to obtain \( k_3 \) by using an approximate value of \( k_4 \) (from Fig. 12 and Table XIII and explanation thereof) and plotting \( R - k_4 \left[ \text{HCrO}_4^- \right]^3 \) versus \( \left[ \text{HCrO}_4^- \right]^2 \), \( k_{-3} \) thus obtained equals \( 5.8 \, \text{M}^{-1} \, \text{sec}^{-1} \) (Fig. 11, Table XII). These two values of \( k_3 \) can be compared to that reported by Schwarzenbach and Meier (1 \, \text{M}^{-1} \, \text{sec}^{-1} \), Reference 30), Swinehart and Castellan (1.8 \, \text{M}^{-1} \, \text{sec}^{-1} \), Reference 16) and Hoyer and Baldwin (0.8 \, \text{M}^{-1} \, \text{sec}^{-1} \), Reference 18) and it shows reasonable agreement in view of the wide range of ionic strengths encompassed by these different studies.

Both Schwarzenbach and Meier and Swinehart and Castellan used the potassium salt in contrast to the sodium salt used in this study. The former investigators used a continuous flow method while the latter employed a relaxation technique studying the kinetics of the chromate-dichromate conversion by a concentration-jump method.

Below pH 7, the dependence of \( [\text{H}^+] \) is first order and of \( [\text{HCrO}_4^-] \) is third, therefore it is apparent that below pH 7, some path or paths third order in \( [\text{HCrO}_4^-] \) are important. The simplest schemes available are:

\[ (iv) \, \text{HCrO}_4^- + \text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons{k_4} \text{Cr}_3\text{O}_10^{2-} + \text{OH}^- \quad \text{or} \]
\[ (v) \, \text{HCrO}_4^- + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \xrightleftharpoons{k_5} \text{Cr}_3\text{O}_10^{2-} + \text{H}_2\text{O} \]
Figure 10 PLOT OF $\frac{R}{[\text{HCrO}_4^-]^2}$ vs $[\text{HCrO}_4^-]$ FOR THE DETERMINATION OF $k_3$ AND $k_4$

$R = \frac{[\text{HCrO}_4^-]^2}{[\text{HCrO}_4^-]}$
Figure 11: PLOT OF ($R - R_0$) vs $\left[\text{HCrO}_4^-\right]^2$ FOR THE DETERMINATION OF $k_3$
Figure 12 PLOT OF $\frac{R-R_3}{[HCrO_4^-]^3}$ vs $[H^+]$

TO OBTAIN $k_4$ AND $k_5$

$R_3 = k_3 [HCrO_4^-]^2$
Equation (v) is also consistent with the following:

a) \( \text{HCrO}_4^- + \text{HCr}_2\text{O}_7^- \rightleftharpoons \text{Cr}_3\text{O}_{10}^2^- + \text{H}_2\text{O} \)

b) \( \text{H}_2\text{CrO}_4 + \text{Cr}_2\text{O}_7^- \rightleftharpoons \text{Cr}_3\text{O}_{10}^2^- + \text{H}_2\text{O} \)

Since (a) and (b) are kinetically indistinguishable, we will consider only (a). Therefore

\[
R = k_{-3}[\text{HCrO}_4^-]^2 + k_4[\text{HCrO}_4^-][\text{Cr}_2\text{O}_7^-]^2 + k_5[\text{HCrO}_4^-][\text{Cr}_2\text{O}_7^-][\text{H}^+]
\]

\[
= k_{-3}[\text{HCrO}_4^-]^2 + k_4K_2[\text{HCrO}_4^-]^3 + k_5K_2[\text{HCrO}_4^-]^3[\text{H}^+]
\]

\[
R = k_{-3}[\text{HCrO}_4^-]^2
\]

When \( \frac{[\text{HCrO}_4^-]}{[\text{HCrO}_4^-]^3} \) is plotted against \([\text{H}^+]\), the slope gives the value of \( k_4K_2 \) with an intercept equal to \( k_5K_2 \).

(Fig. 12 and Table XIII)

The values of \( k_4 \) and \( k_5 \) are obtained from least-squares fits of the data for the \( \text{HClO}_4 \) and \( \text{HAc} - \text{NaAc} \) systems:

\[ k_4K_2 = 1100 \text{ M}^{-2} \text{ sec}^{-1} \] and \( k_4 = 15.7 \text{ M}^{-2} \text{ sec}^{-1} \)

\[ k_5K_2 = 5.89 \times 10^9 \text{ M}^{-3} \text{ sec}^{-1} \] and \( k_5 = 843 \times 10^7 \text{ M}^{-3} \text{ sec}^{-1} \)

The very close agreement of \( k_4K_2 \) value obtained by this method as an intercept and the method described in page 54 from the slope (950 M\(^{-2}\) sec\(^{-1}\)) further substantiates the proposed mechanisms.

It can be seen from this graph that points below pH 4.90 deviate from the straight line towards a lower value. This means that the value of \( R \) in

\[
R = k_{-3}\left(\frac{[\text{HCrO}_4^-]^2}{[\text{HCrO}_4^-]^3}\right)
\]
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TABLE XIII
DATA FOR THE DETERMINATION OF \( k_4 \) and \( k_5 \)

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(Series B)

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(Series G)

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may be too small, and as mentioned before, this may be due to inefficiency of the flow machine in providing complete mixing for the very fast reaction at low pH's.

A plot of log R calculated from the equation

\[ R = k_{-3}[HCrO_4^-]^2 + k_4K_2[HCrO_4^-]^3 + k_5[HCrO_4^-]^3[H^+] \]

against \(-\log[H^+]\) is shown in Fig. 13. The experimental results follow the calculated curve closely except for points below pH 4.90, where inefficient mixing is presumed to cause this discrepancy.

The three proposed mechanisms of exchange have the following experimental support: the very close agreement between the rate of exchange \(R\) calculated from derived \(k'\)'s with observed rates of exchange; agreement of the derived rate constant \((k_{-3})\) with those obtained from other kinetic studies using different physical methods.

From Fig. 13, it can be seen that at pH 7.6 - 8.4 mechanism (iii) is predominant, at pH 6.7 - 7.6 mechanism (iv) is important, at pH below 6.0 mechanism (v) is important, while both (iv) and (v) are operating between pH 6.70 - 6.00.

Hoyer and Baldwin (18) suggested that the exchange of oxygen-18 between water and chromium (VI) oxyanions at pH above 7 is a bimolecular substitution reaction. The formation of dichromate ion can be pictured as

\[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
1 & 0 & 0 \\
\end{bmatrix}_{2-} + \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}_{-} \rightleftharpoons \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}_{3-}
\]
Figure 13  A COMPARISON OF THE ACID DEPENDENCE OF OXIDIZED WITH CALCULATED RATE OF OXYGEN EXCHANGE R. \([\text{Cr(VI)}] = 0.2 \text{M}\)

\[ R_3 = k_3 [\text{HCrO}_4^-]^2 \]
\[ R_4 = k_4 [\text{HCrO}_4^-]^3 \]
\[ R_5 = k_5 [\text{HCrO}_4^-]^3 [\text{H}^+] \]
and for mechanism (iii), they proposed the following

\[ \text{H}_2\text{O} + \left[ \begin{array}{c} 0 \\ \text{Cr} \\ 0 \\ 0 \\ 0 \\ \text{Cr} \\ 0 \\ 0 \end{array} \right]^{2-} \rightarrow \left[ \begin{array}{c} \text{H} \\ 0 \\ \text{O} \\ \text{Cr} \\ 0 \\ \text{Cr} \\ 0 \\ 0 \end{array} \right]^{2-} \]

Both of the above paths involve a five co-ordinated chromium atom in the transition state. A five co-ordinated intermediate for the transition metals has been suggested by Basolo and Pearson (32). They pointed out the larger size of the central element, compared with carbon, will greatly favour a displacement type mechanism in that a fifth group can be held with less steric crowding. Since the fact of inversion on bimolecular substitution has been often demonstrated for the carbon atom, they suggest the intermediate to be a trigonal bipyramid analogous to that of carbon, with the entering group and leaving group lying on the digonal axis. For the activated complex

\[ \left[ \begin{array}{c} \text{H} \\ \text{O} \\ \text{Cr} \\ 0 \\ \text{Cr} \\ 0 \\ 0 \\ \text{Cr} \end{array} \right]^{2-} \]

which is also quoted by Wilkins (15), three oxygen atoms
lie in the trigonal plane and the other two lie on the trigonal axis. The first group of oxygen atoms are loosely bonded to the Cr atom. Calculation shows that the distance between a hydrogen atom bonded to oxygen in the trigonal axis and an oxygen in the trigonal plane is about 2.4 Å. Therefore a hydrogen ion bonded to the second group of oxygen atoms could migrate to the oxygen on the trigonal plane and thus this oxygen might be removed instead of the one in the attacking molecule.

By analogy with the above mechanism proposed for path (iii), the mechanisms for paths (iv) and (v) are now discussed. The reaction is viewed in terms of a nucleophilic attack by HCrO$_4^-$ on Cr$_2$O$_7^{2-}$ leading to the formation of a trichromate ion. A five co-ordinated chromium atom is also postulated and again oxygen exchange is presumed to involve the atoms that lie in the trigonal plane:

\[
\left[\begin{array}{c}
\text{HO} & \text{Cr} & 0 \\
0 & 0 & 0
\end{array}\right]^- + \left[\begin{array}{c}
0 & \text{Cr} & 0 & 0 \\
0 & 0 & 0 & 0
\end{array}\right]^{2-} \xrightarrow{\text{\(\text{\$}\)}}
\]

\[
\left[\begin{array}{c}
\text{OH} & \cdots & 0 & 0 & 0 \\
0 & \text{Cr} & 0 & \text{Cr} & 0 \\
0 & 0 & 0 & 0 & 0
\end{array}\right]^{3-} \xrightarrow{\text{\(\text{\$}\)}}
\]

\[
\left[\begin{array}{c}
0 & \text{Cr} & 0 & \text{Cr} & 0 \\
0 & 0 & 0 & \text{Cr} & 0 \\
0 & 0 & 0 & 0 & 0
\end{array}\right]^{2-} + \left[\begin{array}{c}
\text{OH}^-
\end{array}\right]
\]

path (iv)

This path is consistent with the experimental third
order dependence on \([\text{HCrO}_4^-]\) since the formation of \(\text{Cr}_2\text{O}_7^{2-}\) requires two \(\text{HCrO}_4^-\). In mechanism (v) a first order dependence of \([\text{H}^+]\) was found. The addition of a hydrogen ion to \(\text{Cr}_2\text{O}_7^{2-}\) forms \(\text{HCr}_2\text{O}_7^-\), this extra hydrogen ion makes the atom more positive and hence facilitates the nucleophilic attack.

The much faster rate of exchange in the hydrochloric acid system was quite surprising. This may be due to the formation of a complex, \(\text{CrO}_3\text{Cl}^-\), whose existence was known for many years. X-Ray studies have been reported on \(\text{KCrO}_3\text{Cl}\) (32) and a \(\text{NH}_4\text{CrO}_3\text{Cl}\). Chloro-complexes have been postulated in the mechanism of oxidation of iso-propyl alcohol by \(\text{Cr(VI)}\) in 86.5 % acetic acid and a formation equilibrium quotient has been reported (33). The equilibrium of \(\text{CrO}_3\text{Cl}^-\) in aqueous solutions has been reported by Haight and his co-workers (34) and more recently in detail by Tong and Johnson (35). In both of these studies, the concentration of \(\text{Cr(VI)}\) was very low (approximately \(10^{-5}\) M) and hence the dimeric species were negligible. Both groups used spectrophotometric methods (Beckman DU Spectrophotometer) to determine the equilibrium constant and their results agreed very well.

The reaction was assumed to be as follows:

\[
\text{a) } \text{HCrO}_4^- + \text{Cl}^- \xrightleftharpoons[k_{\text{Cl}^-}]{<} \text{CrO}_3\text{Cl}^- + \text{OH}^- 
\]

However, in the present study, the concentration of \(\text{Cr(VI)}\) is approximately 5000 times greater, hence a number of other reactions must be considered:
b) \[ \text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons{k_{\text{Cl}}} \text{CrO}_3\text{Cl}^- + \text{CrO}_4^{2-} \]

c) \[ \text{Cl}^- + \text{HCr}_2\text{O}_7^- \xrightleftharpoons{} \text{ClCr}_2\text{O}_6^- + \text{OH}^- \]

d) \[ \text{HCrO}_4^- + \text{CrO}_3\text{Cl}^- \xrightleftharpoons{} \text{ClCr}_2\text{O}_6^- + \text{OH}^- \]

(b does not contribute to exchange, so may be neglected).

Experiments were conducted to determine the dependence of the chloride catalyzed exchange on \([\text{HCrO}_4^-]\). The net rate due to the complex was obtained by subtracting the rate of exchange in perchloric acid \(R_{\text{HClO}_4}\) from that in perchloric acid with some added NaCl at a given pH. Dependence of rate on \([\text{HCrO}_4^-]\) or \([\text{Cr}_2\text{O}_7^{2-}]\) was then obtained by holding \([\text{Cl}^-]\) constant and varying Cr(VI). It is not possible to reach a positive conclusion from these experiments. It can be said, since the Cl\(^-\) "catalyzed" portion is 2nd order in HCrO\(_4^-\), the process Cl\(^-\) + HCrO\(_4^-\) \xrightleftharpoons{} ClCrO\(_3^-\) + OH\(^-\) is not rapid enough to account for exchange, although it may contribute to establishment of species equilibrium (along with (c) and/or (d)). The present study suggests the existence of a dimeric Cl\(^-\) containing chromium(VI) species, but offers no evidence regarding its mode of formation ( (c) or (d) ) or concentration.

For path (a):

\[ R_{\text{HCl}} - R_{\text{HClO}_4} = k'_{\text{Cl}} \left[ \text{Cl}^- \right] \left[ \text{HCrO}_4^- \right] \]

for path (c):

\[ R_{\text{HCl}} - R_{\text{HClO}_4} = k''_{\text{Cl}} \left[ \text{Cl}^- \right] \left[ \text{HCr}_2\text{O}_7^{2-} \right] = k''_{\text{Cl}} - K_2 \left[ \text{Cl}^- \right] \left[ \text{HCrO}_4^- \right]^2 \]
When \( \log \frac{R_{HCl} - R_{HClO_4}}{[Cl^-]} \) was plotted against \( \log [HCrO_4^-] \) and \( \log [Cr_2O_7^{2-}] \) respectively (Fig. 14, Table XIV) the following values were obtained,

\[
\begin{align*}
 k_{1}^1 &= 35.5 \text{ M}^{-1} \text{ sec}^{-1} \\
 k_{1}^n &= 40.0 \text{ M}^{-1} \text{ sec}^{-1}
\end{align*}
\]

**TABLE XIV**

**EFFECT OF \([HCrO_4^-]\) AND \([Cr_2O_7^{2-}]\) ON THE RATE OF OXYGEN EXCHANGE AT pH = 6.00**

<table>
<thead>
<tr>
<th>([Cr(VI)])</th>
<th>(\log [HCrO_4^-])</th>
<th>(\log [Cr_2O_7^{2-}])</th>
<th>(R_{HCl+0.003MNaCl} )</th>
<th>(R_{HClO_4})</th>
<th>(R' - R'')</th>
<th>(\log \frac{R' - R''}{[Cl^-]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>-1.506</td>
<td>-1.167</td>
<td>.695</td>
<td>.321</td>
<td>128.0</td>
<td>2.107</td>
</tr>
<tr>
<td>0.16</td>
<td>-1.564</td>
<td>-1.282</td>
<td>.526</td>
<td>.191</td>
<td>111.7</td>
<td>2.048</td>
</tr>
<tr>
<td>0.12</td>
<td>-1.642</td>
<td>-1.439</td>
<td>.307</td>
<td>.095</td>
<td>70.8</td>
<td>1.850</td>
</tr>
<tr>
<td>0.08</td>
<td>-1.752</td>
<td>-1.660</td>
<td>.175</td>
<td>.044</td>
<td>43.7</td>
<td>1.640</td>
</tr>
</tbody>
</table>
Figure 14  PLOT OF $\log \left( \frac{R_t - R_{HCrO_4^-}}{[Cl^-]} \right)$ vs $\log [HCrO_4^-]$ AND $\log [Cr_2O_7^{2-}]$
From the slope (first order with respect to \( \text{Cr}_2\text{O}_7^{2-} \)) and second order with respect to \( \text{HCrO}_4^- \), it can be concluded that path (c) or (d) is responsible for the faster exchange found.

The rate of oxygen exchange in the chloride catalyzed path was found to have a second order dependence on \( \text{HCrO}_4^- \). This is quite unexpected in view of the results of both Tong and Haights group which implies a first order dependence. An explanation for the discrepancy is the large difference in the concentration of Cr(VI) employed. In the present study at pH below 6 and \( [\text{Cr(VI)}] \) equal to 0.2 M, the concentration of the dimeric species is double that of the monomeric species; however, in contrast, the dimeric species is negligible in their investigations due to the very low \( [\text{Cr(VI)}] \) used (1 x \( 10^{-5} \) M).

The author suggests the following mechanistic schemes, for path (c):

\[
\begin{align*}
\text{Cl}^- + \text{HCr}_2\text{O}_7^- & \quad \rightleftharpoons \quad \text{HCrO}_4^- + \text{ClCrO}_3^- \\
\end{align*}
\]

\[
\begin{pmatrix}
\text{HO} & 0 & 0 \\
\text{Cl} - \text{Cr} - 0 - \text{Cr} - 0 \\
0 & 0
\end{pmatrix}^{2-}
\]
for path (d):

\[
HCrO_4^- + CrO_3Cl^- \rightleftharpoons ClCr_2O_6^- + OH^-
\]

\[
\begin{array}{c}
\text{HO} \\
\text{0} \\
\text{0 - Cr - 0 - Cr - Cl} \\
\text{0} \\
\text{0}
\end{array}
\]
REFERENCES


