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I. Title

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A STUDY OF THE OXYGEN EXCHANGE

BETWEEN CHROMATE ION AND WATER

BY

JAMES HSIAO-HSIN CHIANG, 1945-

A THESIS

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Approved by

H. O. McDonald (Advisor)   ~Samir A. Hanna~

~C. Y. Ho~

ABSTRACT

The kinetics of the isotopic exchange reaction between O^{18}-enriched chromate ion and solvent water have been measured as a function of pH and chromate ion concentration. The exchange kinetics can be explained in terms of the dimerization equilibria

$$HCrO_4^- + CrO_4^= \rightleftharpoons Cr_2O_7^= + OH^- \text{ and } 2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$

except at high pH, where it is independent of pH. Rate constants at $30^\circ C$ for the reactions of the dimerization equilibria and the first order reaction at the high pH have been evaluated from the exchange results. The activation energy of the exchange at pH 8.70 and 0.15$\underline{M}$ chromate ion is 11,500 cal mole^{-1}. The reaction proceeds faster in D_2O with R_D/R_H equal to 1.64 at pH 7.2. The experimental results are compared with the values obtained by other investigators.

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ACKNOWLEDGEMENT

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I. INTRODUCTION

The importance of heavy oxygen as a means of investigating the mechanism of certain reactions was recognized soon after its discovery. The possibilities of oxygen exchange between water and oxyanions such as $SO_4^=$, $PO_4^{\equiv}$, $AsO_4^{\equiv}$, MnO_4^-, NO_3^-, ClO_4^-, ClO_3^-, $CO_3^=$ and $CrO_4^=$ have been investigated.[1][2][3][4]

Each oxyanion contains a central atom in a positive oxidation state, surrounded by oxide ions or hydroxide ions. The rate of oxygen exchange between water and oxyanions is a function of several factors:[1]

A. The acidity of the media used.

B. The size of the central atom of the oxyanion.

C. The electronegativity of the central atom of the oxyanion.

D. The oxidation state of the central atom of the oxyanion.

The rate of oxyanion exchange reactions is generally dependent upon the acidity of the media, for the rate generally increases strikingly with increased hydrogen ion concentration. Another important factor on the rate of oxyanion exchange reactions is the oxidation state of the central atom. In cases of elements that form oxyanions in more than one oxidation state, it is found that the rates for the lower oxidation state are faster than those for the higher oxidation state, as evidenced by the rate

of oxygen exchange of $ClO^->ClO_2^->ClO_3^->ClO_4^-$ previously reported.[3] Within a period of the periodic table it is generally true that rates of replacements decrease as the charge increases from left to right, as $H_2SiO_4^=$, $HPO_4^=$, $SO_4^=$ and ClO_4^-. It is reasonable that the strength of the oxygen-to-central-atom bond should increase as the charge on the central atom increases. In any family of the periodic table, the rates of replacement increase as the size of the central-atom increases. This is to be expected, since the strength of the oxygen-to-central-atom bond decreases as size increases; the rates of oxygen exchange have been reported: $ClO_3^-<BrO_3^-<IO_3^-$.[2]

The system composed of the oxyanions of chromium(VI) in aqueous solution and their interactions with hydronium and hydroxide ions has been the subject of several types of investigation. The rapid hydrolysis or neutralization of dichromate ion solutions has been the subject of several studies utilizing flow techniques.[5][6][7][8] The kinetics of the monomer-dimer equilibrium was further studied by a relaxation method by Swinehart and Castellan.[9] Another investigative approach is the measurement of the exchange of isotopic oxygen between chromate(VI) oxyanions and solvent water. This method offers the advantage of studying the system at chemical equilibrium with the rate of isotopic exchange reflecting the rates of all processes resulting in exchange. From the early studies,[10][11][12][13] there were no data reported on

the activation energy and the deuterium isotope effect on the rate of oxygen exchange between the chromium(VI) oxyanion and solvent water.

The present work includes data not only on the effect of chromium(VI) oxyanion concentrations and pH on the rate of oxygen exchange, but also evaluates the possible mechanisms proposed for the hydrolysis of dichromate as well as for the oxygen exchange of the chromate ion. The activation energy and the deuterium isotope effect on the rate of the oxygen exchange between the chromate ion and water is used to evaluate the mechanism.

II. REVIEW OF LITERATURE

Early attempts of the study of the heavy oxygen reactions had been reviewed by Rietz and Day.[14][15] The work done by Mills in general showed that the effect of alkali is to retard greatly but not eliminate the reaction of the oxygen exchange between chromate ion and water. He reported that at $19.3^\circ C$, the half-time for the oxygen exchange of sodium chromate and water is 4.5 hours.[16] In Mills' work, the method of density measurement was used; however, this method does not permit exact determinations of isotopic composition.

In 1940, several investigators found that the half-time of oxygen exchange for sodium chromate and potassium chromate with O^{18}-water, at $100^\circ C$, in neutral or alkaline solution, is about 24 hours, but in a neutral solution of chromate at $20^\circ C$, the exchange proceeds at a faster rate; the half-time is about 4.5 hours.[17] In the presence of caustic alkali at $20^\circ C$, however, there is no measureable exchange in 240 hours. This retardation by alkali is thought to be due to the equilibrium reaction

$$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^-. \quad [17]$$
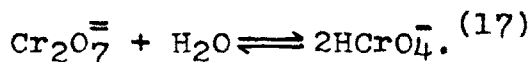
At the same time, Hall and Alexander found that in the case of sodium chromate, the half-time may be about 5 minutes or less at $100^\circ C$.[11] From those early investigations, mechanisms involving formation of dichromate have been suggested as: $K_2CrO_4 + H_2O \rightleftharpoons 2K^+ + OH^- + HCrO_4^-$

followed by $2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$

No data were available as to the effect of chromate ion concentration on the rate of oxygen exchange of chromates until the publication of the work by Baloga and Earley.[12] They stated that the rate of oxygen exchange between chromate and water in moderately alkaline solution is first order in $CrO_4^=$ concentration and independent of pH. The first-order rate constant at $25^\circ C$ in $1\underline{M}$ $LiClO_4$ is $(6.9 \pm 0.1) \times 10^{-4}$ min^{-1}. Below pH 9.7, the rate is pH dependent; at pH 7.2 the rate is second order in chromate ion concentration indicating a mechanism involving $Cr_2O_7^=$.

In another report,[18] several oxy-species and equilibria that can exist in aqueous solutions of Cr(VI) dependent upon the pH were reported:

$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^-$ $K_{25^\circ}{}_{(\mu=3)} = 10^{-2.2}$, $K_{25^\circ}{}_{(\mu=0)} = 10^{-1.6}$

$Cr_2O_7^= + OH^- \rightleftharpoons HCrO_4^- + CrO_4^=$

$HCrO_4^- + OH^- \rightleftharpoons CrO_4^= + H_2O$

$HCrO_4^- \rightleftharpoons CrO_4^= + H^+$ $K_{25^\circ}{}_{(\mu=3)} = 10^{-5.9}$, $K_{25^\circ}{}_{(\mu=0)} = 10^{-6.5}$

$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$ $K_{25^\circ}{}_{(\mu=1)} = 4.2, 5.0$
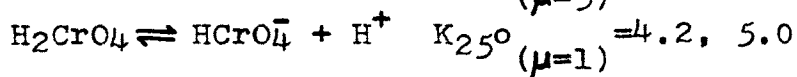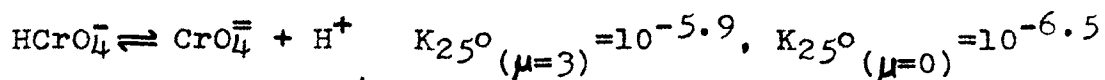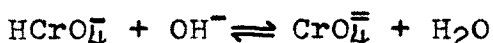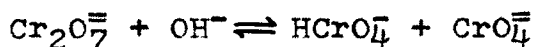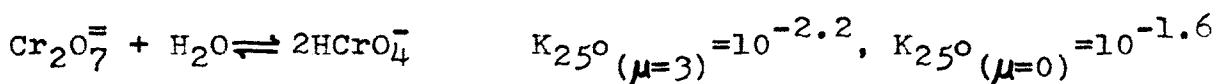
The investigators reported that above pH 8, only $CrO_4^=$ ions exist, whereas in the pH 2 to 6 range, $HCrO_4^-$ and $Cr_2O_7^=$ ions are in co-equilibrium. At pH $\leq$ 1, other species such as H_2CrO_4 may exist.

The most recent study on the oxygen exchange between $CrO_4^=$ and water was done by Holyer and Baldwin.[13] They

determined the rate of oxygen exchange between O^{18}-enriched chromate ion and water as a function of pH and the total chromate ion concentration. They also concluded that the exchange can be explained in terms of the dimerization equilibria:

$$HCrO_4^- + CrO_4^= \rightleftharpoons Cr_2O_7^= + OH^-$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$
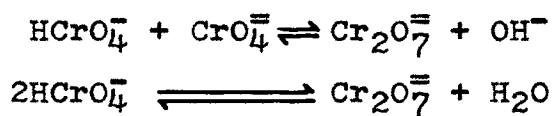
except at high pH, where a slow pH-independent exchange was reported and the process is:

$$CrO_4^{*=} + H_2O \rightleftharpoons CrO_4^= + H_2O^*$$

III. EXPERIMENTAL

A. Preparation of O^{18}-Enriched Sample:

O^{18}-tagged sodium chromate was prepared by dissolving C.P. grade sodium chromate in water enriched to about 1.5% in O^{18} (Obtained from International Chemical & Nuclear Corp. Chemical & Radio-isotope Division, Irvine, Calif.) for more than twenty-four hours at 30°C. The resulting solution contained the enriched sodium chromate. This solution was then cooled in ice and vacuum distilled to obtain the O^{18}-enriched sodium chromate which was then recrystallized from the solution.

B. Preparation of Solutions for the Kinetic Runs:

The oxygen exchange between the enriched sodium chromate and solvent water was found to proceed by three paths depending on the acidity. Stock solutions of $HClO_4$ (0.1$\underline{N}$) and NaOH (0.1$\underline{N}$) were prepared. Solid enriched sodium chromate was dissolved in distilled water containing the calculated amount of 0.1$\underline{N}$ $HClO_4$ or 0.1$\underline{N}$ NaOH to give the desired pH and having a concentration of $LiClO_4$ calculated to bring the total ionic strength to $\mu=1$. This solution was then put into the water bath at constant temperature (30 $\pm$ 0.02)$^{\circ}$ C.

C. Outline of a Kinetic Exchange Experiment:

1. Chromate Ion-Water Exchange:

A typical exchange solution was prepared by weighing a known amount of solid enriched sodium chromate into a

volumetric flask containing a previously standardized
$HClO_4$ (or NaOH) -$LiClO_4$ solution with the desired pH and
ionic strength at a certain constant temperature. The pH
was determined by using the Beckman Zeromatic direct-
reading pH meter. Samples of the exchange reaction were
pipetted, at predetermined time-intervals, into centri-
fuge tubes which contained $0.1\underline{N}$ $Pb(NO_3)_2$ solution for pre-
cipitating the chromate and thereby quenching the exchange.
The precipitates were then centrifuged, washed and re-
centrifuged, and finally oven-dried below $100^{\circ}C$. The
dried samples were mixed with graphite, rolled in Molyb-
denum foils, clamped in the holders as shown in Figure 1
and connected to a vacuum system. A sample bulb was con-
nected to the vacuum system and the entire system was
evacuated to 10^{-5} mm Hg or lower. When this pressure was
reached, the system was shut off from the vacuum pump and
the foil containing the sample was heated by means of an
electric current. The evolved CO_2 was then frozen out
into the freezing tip of the furnace with liquid air. Any
gases not condensed were pumped off and after a suitable
vacuum was reached, the CO_2 was then allowed to expand
into the sample bulb. There were other gases present
besides CO_2 but none interfered with the isotopic analysis.

    2. Time Measurement:

The exchange rates for the exchange of oxygen between
chromate ion and water were found to be moderately fast at

TO COLD TRAP AND
VACUUM PUMP

TO THERMOCOUPLE GAUGE

HI-VAC STOPCOCK

10/30 $

Na_2CrO_4 AND
GRAPHITE
MIXTURE
ROLLED IN
MO FOIL

TUNGSTEN TO
PYREX SEAL

FREEZING
TIP

10/30 $

TO SAMPLE BULB
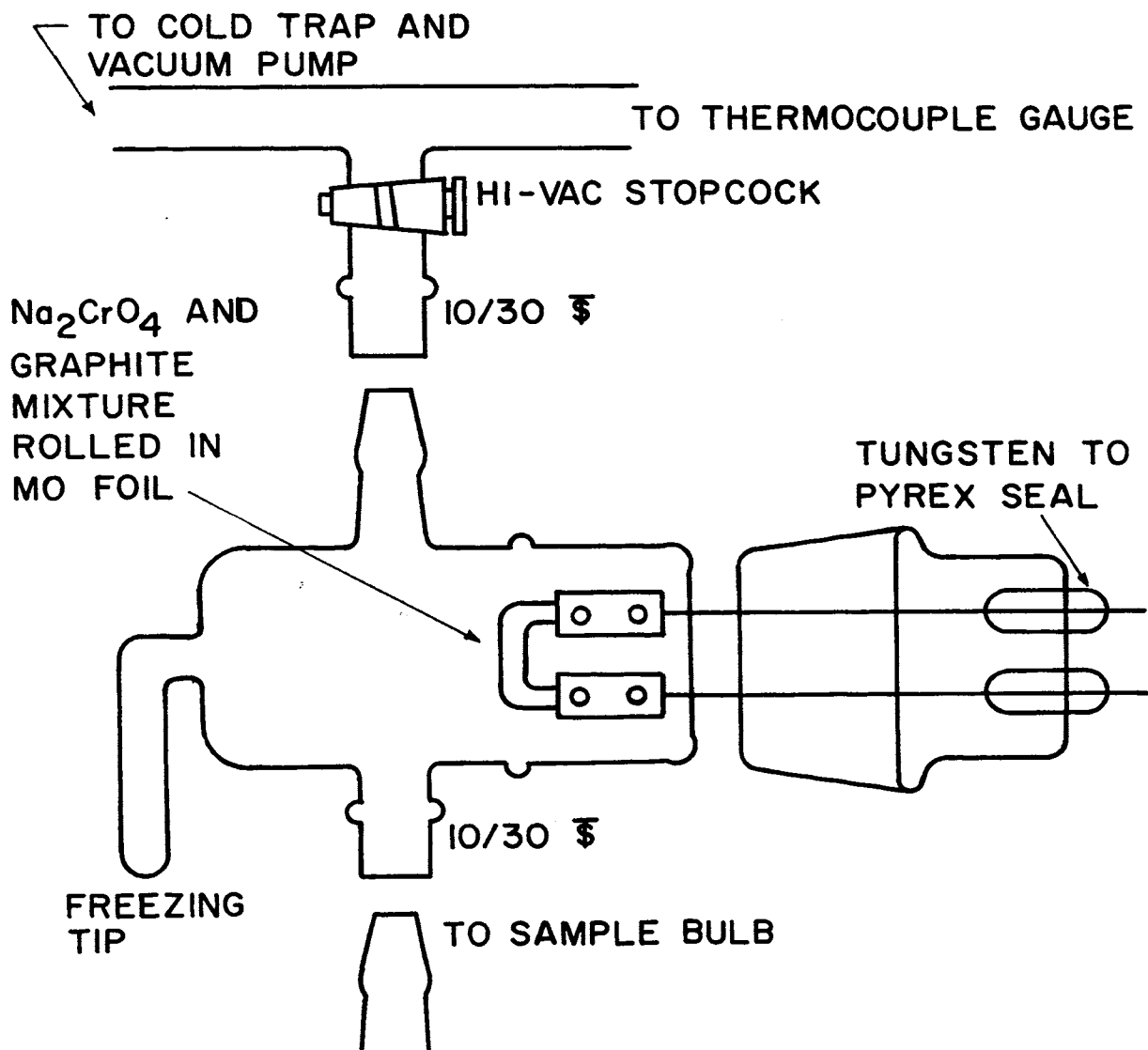
Figure 1.   Furnace

room temperature and in acidic solutions. It was found that during the preparation of an exchange solution, some exchange occurred. Thus, the zero time taken for all the exchange studies was that for the first sample taken. Infinite time samples were taken after several half-lives had elapsed and the isotope ratios found compared, within experimental error, with the isotopic ratio found for tank CO_2 which was used as the standard. Since this was so in many cases, the isotopic ratio for tank CO_2 was sometimes taken as the value for the infinite time sample.

3. Isotope Ratio Measurement:

The oxygen isotope exchange ratio of CO_2 was evaluated from the CO_2 peaks. The ion currents of m/e (mass/charge) 46 and 44 were measured separately by means of a Mat Beschreibung Mass Spectrometer Model GD150. The m/e value of 46 corresponds to the ion current of $C^{12}O^{16}O^{18+}$ and that of 44 to the ion current of $C^{12}O^{16}O^{16+}$. The ratio that is measured is expressed by:

$$\text{ratio of } \frac{46}{44} = \frac{(C^{12}O^{16}O^{18+}) + (C^{12}O^{17}O^{17+}) + (C^{13}O^{16}O^{17+})}{(C^{12}O^{16}O^{16+})}$$

$$\text{or ratio of } \frac{46}{44} = \frac{(C^{12}O^{16}O^{18+})}{(C^{12}O^{16}O^{16+})}$$

since the amount contributed by $(C^{12}O^{17}O^{17+})$ and $(C^{13}O^{16}O^{17+})$ is very small.

4. Treatment of Data:

The half-time of exchange was determined by making a plot of log $(1 - F)$ vs. time t, where F is defined as the

fraction exchange. F is calculated by the equation:

$$F = \frac{O_o^{18} - O_t^{18}}{O_o^{18} - O_\infty^{18}}$$

where, O_t^{18} = atom fraction in $CrO_4^=$ or water at time t.

O_o^{18} = atom fraction in $CrO_4^=$ or water at time 0.

O_∞^{18} = atom fraction in $CrO_4^=$ or water at time ∞.

The rate of the reaction leading to exchange was calculated using the equation.[19][20]

$$R = \frac{4(CrO_4^=)(H_2O)}{4(CrO_4^=) + (H_2O)} \times \frac{0.693}{t_{\frac{1}{2}}}$$

where the quantities in parentheses are concentration in formula weight per liter.

D. Results:

1. The Chromate Ion-Water Exchange:

Typical data for the oxygen exchange between chromate ion and water are shown in Table I. By plotting log (1 - F) vs. time and using the equation as described under the section of treatment of data, the rates of the exchanges can be evaluated. A typical plot is shown in Figure 2. All of the experimental results of the rates of oxygen exchange between $CrO_4^=$ and water at 30°C are shown in Table II.

2. The Proposed Reaction Mechanisms:

Since the rate is dependent on both chromate ion concentration and hydrogen ion concentration, the relationships among the rate, chromate ion and hydrogen ion concentrations can be obtained by plotting the rate against the chromate ion concentration at constant pH value and

the hydrogen ion concentration at constant chromate ion concentration. Those data are shown in Tables III and IV. The plots of chromate ion concentrations against constant pH are shown in Figure 3. The plots of hydrogen ion concentrations against constant chromate ion is shown in Figure 4. The slopes of the lines reflect the order of exchange with respect to chromate and hydrogen ion respectively. So, from Figures 3 and 4 the results of the rate dependence on the concentrations of chromate ion and hydrogen ion are:

$$R \propto (\text{H+})^{0.09} (Cr(VI))^{1.1} \qquad \text{pH} > 10$$

$$R \propto (\text{H+})^{1.21} (Cr(VI))^{1.98} \qquad \text{pH} \quad 8\text{--}10$$

$$R \propto (\text{H+})^{1.72} (Cr(VI))^{2.13} \qquad \text{pH} < 8$$

3. The Activation Energy:

The activation energy was calculated for the exchange at pH 8.7 and 7.2. The concentration of sodium chromate was 0.15$\underline{M}$ and 0.20$\underline{M}$, respectively. The exchange rates were measured at 25°, 30°, 35°, 40° and 50°. The results are listed in Tables V and VI and plots of the logarithm of rate versus the reciprocal of the absolute temperature are given in Figures 5 and 6. The slopes of the lines in Figures 5 and 6 give the Arrhenius activation energy, E_a, by the relationship:

$$\text{slope} = \frac{d(\log R)}{d(1/T)} = \frac{d(\log k)}{d(1/T)} = - \frac{E_a}{2.303 \times R'}$$

where R' is the gas constant and T is the absolute temperature. The Arrhenius activation energies are calculated

Table I. Typical Data for the Chromate-Water Exchange

$$Na_2CrO_4 = 0.18M$$

$$T = 30^\circ C$$

$$\mu = 1$$

$$pH = 7.20$$

Sample No.	Time(min)	46/44 ratio	1 - F
44	8	0.00627	1
45	13	0.00612	0.93
46	18	0.00592	0.835
47	23	0.00572	0.740
48	28	0.00563	0.699
49	∞	0.00415	---

$t_{\frac{1}{2}} = 37$ min.

$R \cong 8.04 \times 10^{-1}$ g-atom-oxygen $l^{-1} hr^{-1}$
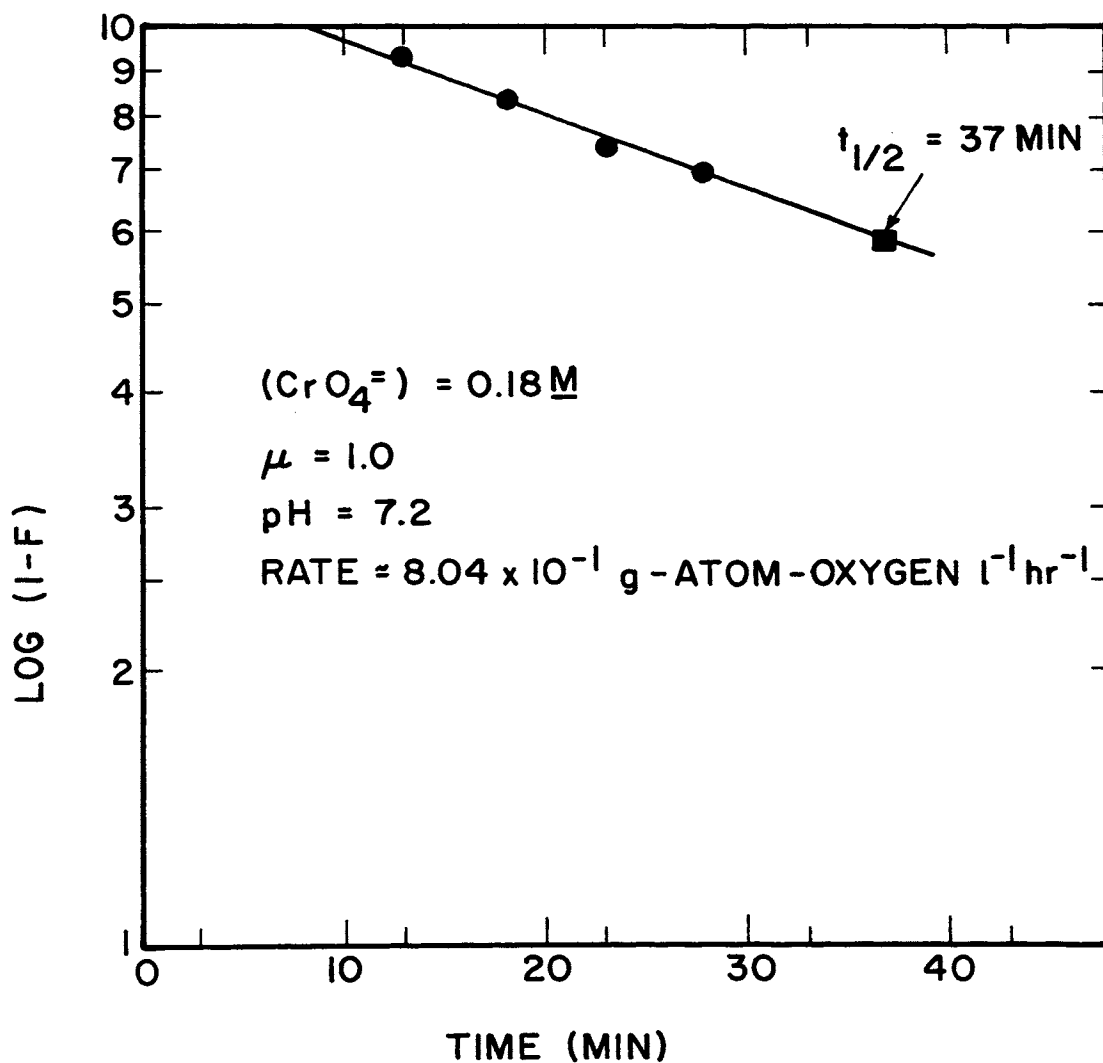
Figure 2. Typical Graph for Determination of the Half-
Life of Exchange and the Rate Constant
at 30°C.

Table II. Rates of Oxygen Exchange Between Chromate Ion
and Water at 30°C

$(CrO_4^=)$, M	pH	$t_{\frac{1}{2}}$	R (g-atom-oxygen $l^{-1}hr^{-1}$)
0.15	11.80	342 hrs.	1.22×10^{-3}
	10.50	260 hrs.	1.60×10^{-3}
	9.80	192 hrs.	2.16×10^{-3}
	8.70	530 min.	4.73×10^{-2}
	6.65	3.5 min.	7.132
0.18	11.15	295 hrs.	1.70×10^{-3}
	10.50	216 hrs.	2.31×10^{-3}
	7.20	37 min.	8.04×10^{-1}
0.20	10.50	214 hrs.	2.60×10^{-3}
	8.70	405 min.	8.24×10^{-2}
	7.20	33 min.	1.008
0.25	10.50	210 hrs.	3.29×10^{-3}
	8.70	325 min.	1.30×10^{-1}
	7.20	26 min.	1.602

Table III. Values of log (Rate of Exchange) Obtained from Data of Table I at Constant pH

pH	(Cr(VI)),$\underline{M}$	log R
10.50	0.15	-2.7959
	0.18	-2.6364
	0.20	-2.5850
	0.25	-2.4802
8.70	0.15	-1.3251
	0.20	-1.0841
	0.25	-0.8861
7.20	0.18	-0.0947
	0.20	-0.0033
	0.25	0.2096
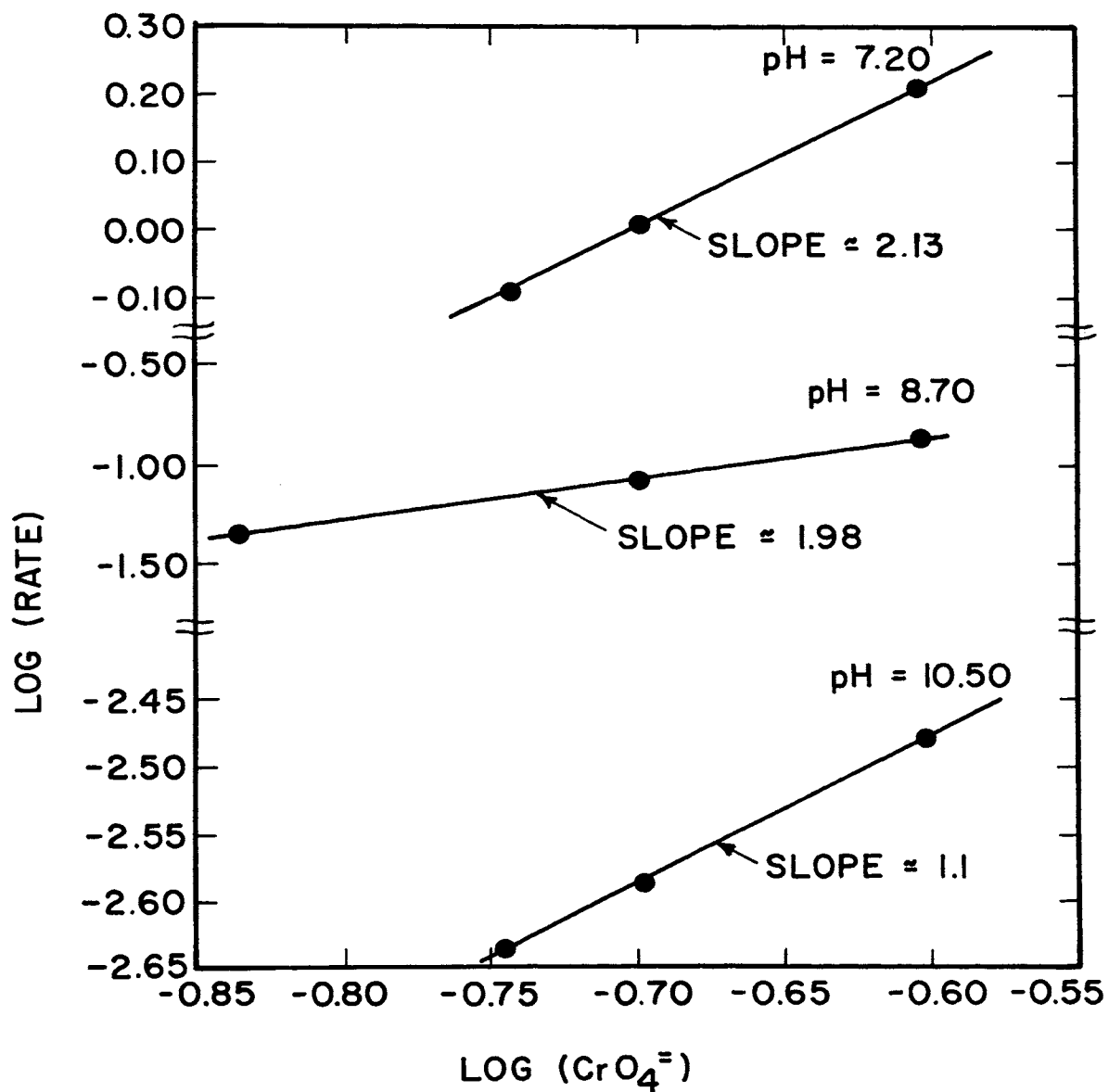
Figure 3. Dependence of the Rate of Oxygen Exchange Between Chromate Ion and Water on Chromate Ion Concentrations.

Table IV. Dependence of Rate of Exchange on

Hydrogen Ion Concentration at

Constant Chromate Ion Concentration

$(CrO_4^=), \underline{M}$	pH	log R
0.15	11.80	-2.9136
	10.50	-2.7959
0.18	11.15	-2.7696
	10.50	-2.6364
0.15	9.80	-2.6655
	8.70	-1.3251
0.15	7.20	-0.0947
	6.65	0.8532
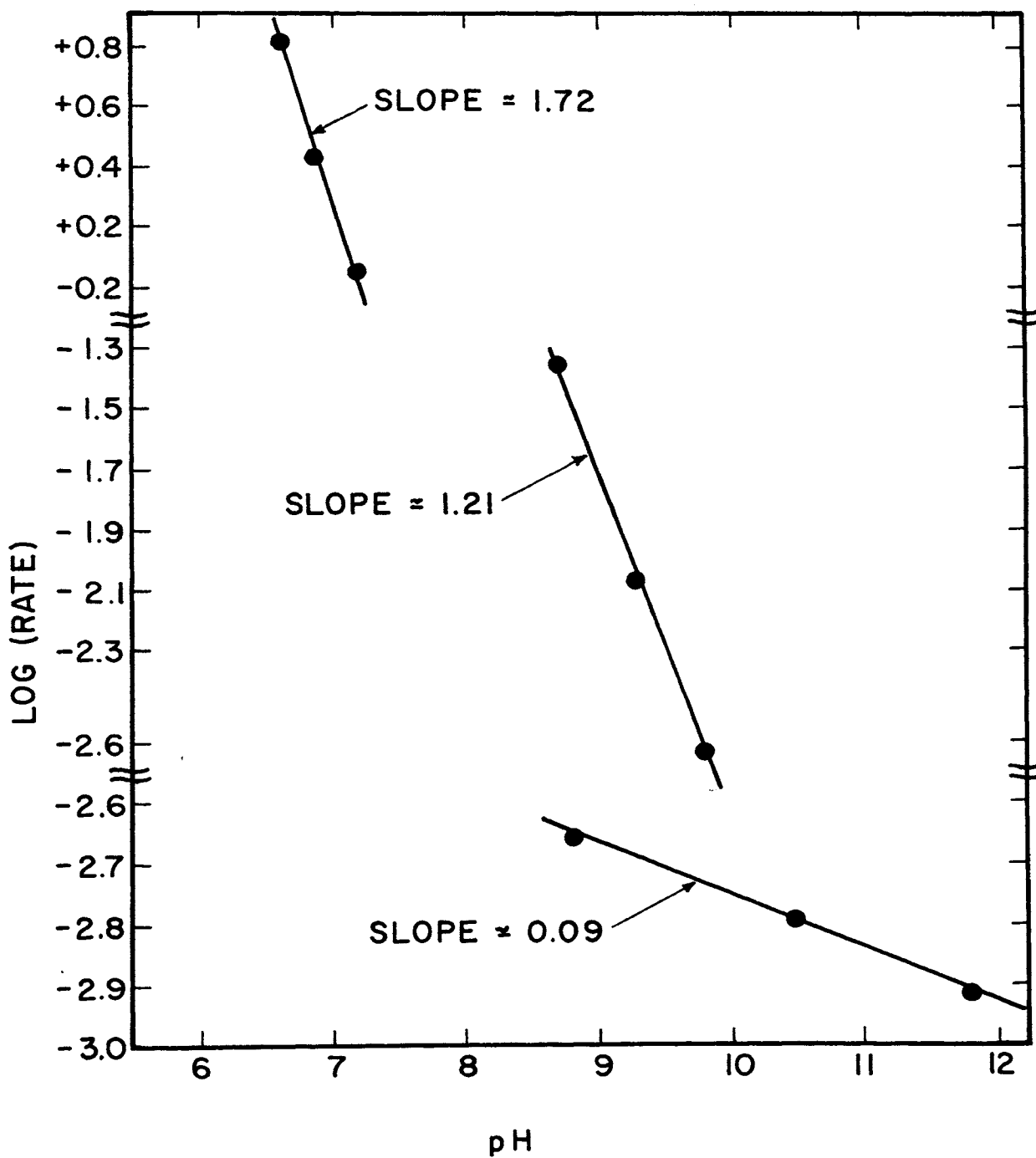
Figure 4. Dependence of the Rate of Oxygen Exchange Between Chromate Ion and Water on Hydrogen Ion Concentrations.

Table V. Experimental Data for the Determination

of Activation Energy at pH 8.7

$$CrO_4^= = 0.15 \underline{M}$$

$$pH = 8.70$$

Experiment No.	Temperature, $^{\circ}C$	Rate*
20	25	3.58×10^{-2}
4	30	4.73×10^{-2}
21	35	6.43×10^{-2}
22	40	8.75×10^{-2}
23	50	1.67×10^{-1}

* Rate in g-atom-oxygen $l^{-1}hr^{-1}$.
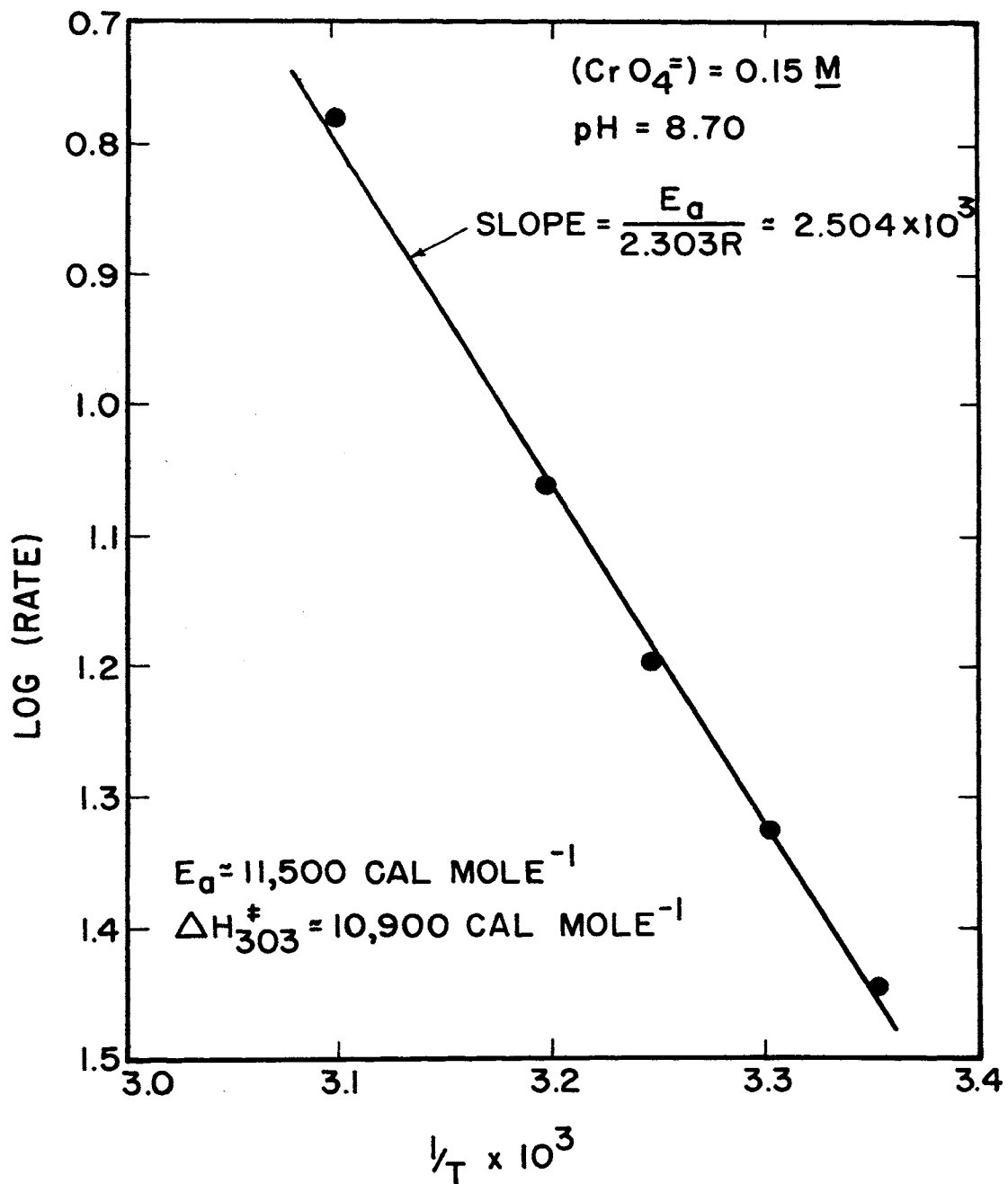
Figure 5. Determination of Activation Energy for the
Exchange of Oxygen Between Chromate Ion
and Water.at pH 8.7.

Table VI. Experimental Data for the Determination

of Activation Energy at pH 7.2

$$CrO_4^{=} = 0.20 \ \underline{M}$$

$$pH = 7.20$$

Experiment No.	Temperature, ^{o}C	Rate*
24	20	0.527
11	30	1.008
25	35	1.351
26	40	1.851
27	50	3.480

* Rate in g-atom-oxygen $l^{-1} \ hr^{-1}$.
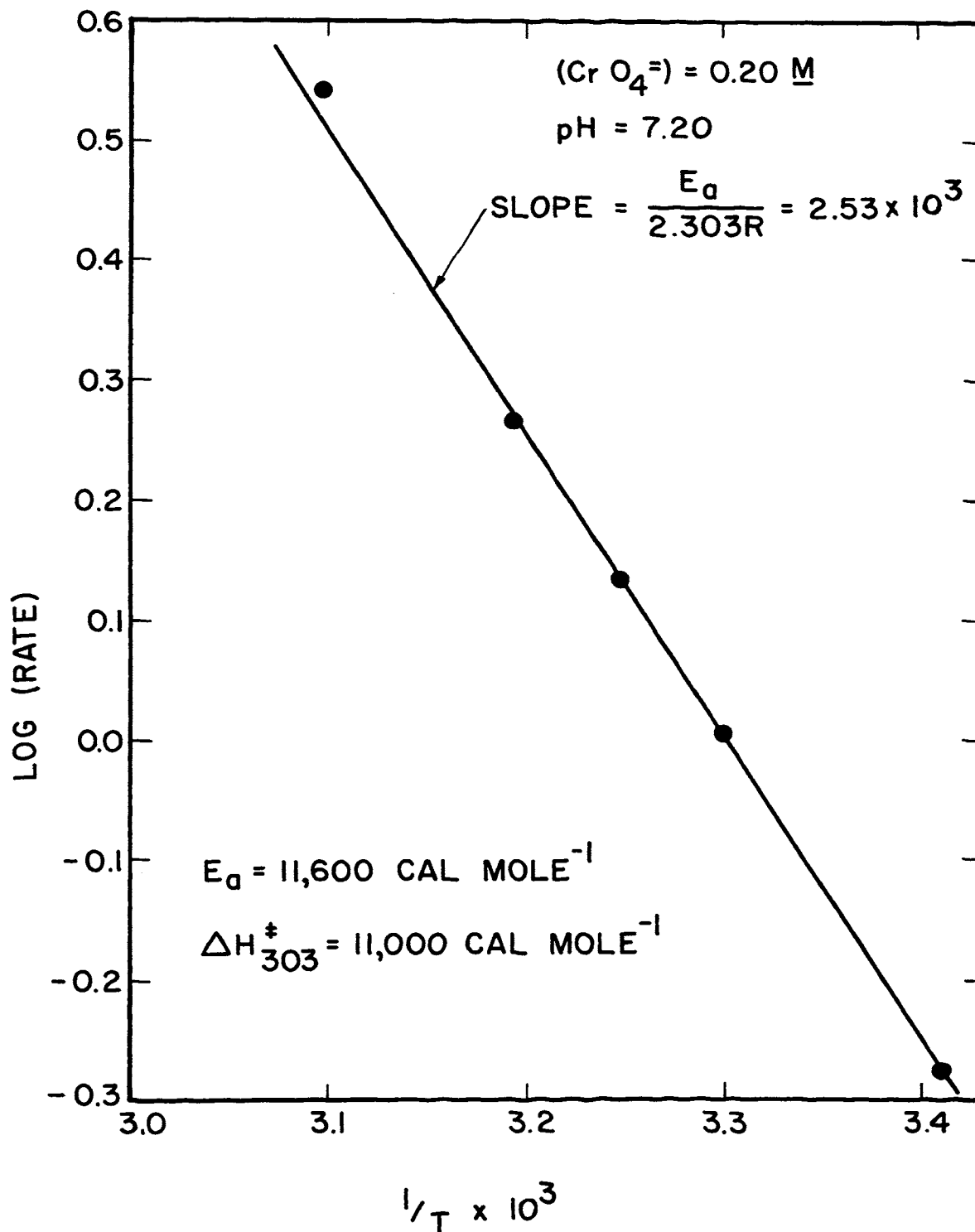
Figure 6. Determination of Activation Energy for the Exchange of Oxygen Between Chromate Ion and Water at pH 7.2.

to be 1.15×10^4 cal mole^{-1} for a chromate ion con-
centration of $0.15\underline{M}$ and a pH of 8.7, and to be 1.16×10^4
cal mole^{-1} for a chromate ion concentration of $0.20\underline{M}$ and
a pH of 7.2. The heat of activation, $\Delta H^{\ddagger}$, is given by:

$$\frac{d(\log R)}{d(1/T)} = - \frac{\Delta H^{\ddagger} + R' T}{2.303 \times R'}$$

The heat of activation was calculated to be 10,900 cal
mole^{-1} at 30°C for $0.15\underline{M}$ chromate ion concentration and
a pH of 8.7; and to be 11,000 cal mole^{-1} at 30°C for
$0.2\underline{M}$ chromate ion concentration and a pH of 7.2.

4. The Isotope Effect:

The rates of the oxygen exchange were studied in
ordinary water and in deuterium oxide. The results are
given in Table VII. The exchange reaction proceeded
faster in D_2O at pH 7.20 solution and proceeded slower
in D_2O for the solution at pH 8.70. The ratios obtained
are:

$$R_D/R_H = 0.71 \quad \text{at pH} = 8.70$$
$$R_D/R_H = 1.64 \quad \text{at pH} = 7.20$$

Table VII.   The Rate of Oxygen Exchange in D_2O

and in H_2O at $30^{\circ}C$

Solvent	$(CrO_4^=)\underline{M}$	pH	$t_{\frac{1}{2}}$,min.	Rate*
D_2O	0.20	8.7	570	5.83×10^{-2}
H_2O	0.20	8.7	405	8.24×10^{-2}
D_2O	0.20	7.2	21	1.648
H_2O	0.20	7.2	33	1.008

* Rate in g-atom-oxygen l^{-1} hr^{-1}.

IV. DISCUSSION

A. Proposed Reaction Mechanisms:

From the experimental results, three possible mechanisms can be formulated which are consistent with the observed rate law for the solutions of pH values higher than 10.

Mechanism I:

$CrO_4^= + H_2O \xrightleftharpoons[k_{-1}]{k_1} \left[\ldots \right]^=$ rapid and reversible

$$\left[\ldots \right]^= \xrightarrow{k_2} CrO_3^= + 2OH^-$$ rate-determining

$CrO_3^= + H_2O^* \longrightarrow H_2CrO_3O^*$ rapid

$H_2CrO_3O^* + 2OH^- \longrightarrow CrO_3O^{*=} + 2H_2O$ rapid
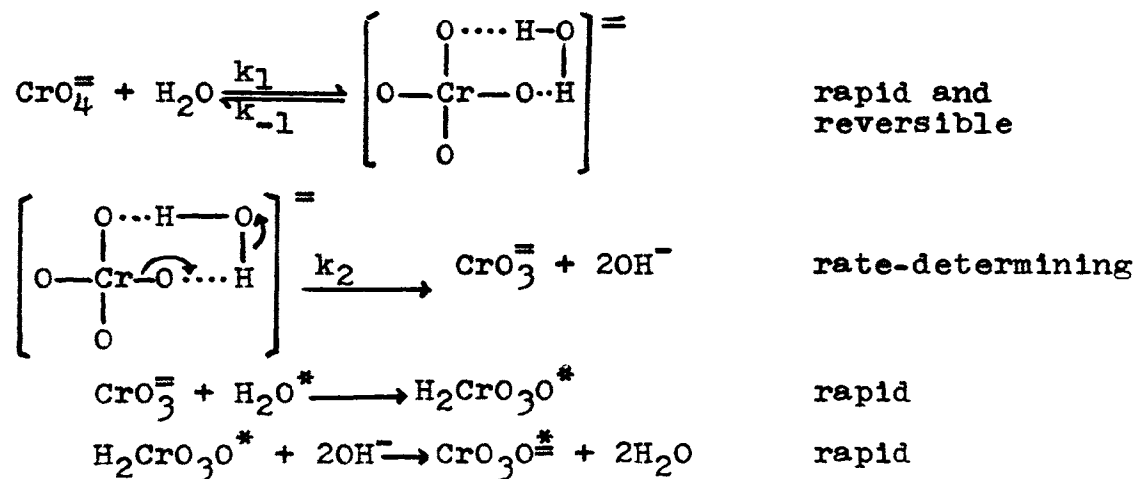
The overall equation yields the following rate law:

$$R = k_2 \frac{k_1}{k_{-1}} (CrO_4^=)(H_2O)$$

Mechanism II:

$CrO_4^= + H_2O^* \xrightleftharpoons[k'_{-1}]{k'_1} \left[\ldots \right]^=$ rapid and reversible

$$\left[\ldots \right]^= \xrightarrow{k_3} HCrO_3O^{*=} + OH^-$$ rate-determining

$HCrO_3O^{*=} + OH^- \longrightarrow CrO_3O^{*=} + H_2O$ rapid

$$R = k_3 \frac{k'_1}{k'_{-1}} (CrO_4^=)(H_2O^*)$$

Mechanism III:

$$CrO_4^= + H_2O^* \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \left[O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle |}{\underset{\displaystyle |}{Cr}}}}-O\cdots H \begin{array}{c} O\cdots H-O^* \\ | \\ \end{array} \right]^= \qquad \text{rapid and reversible}$$

$$\left[O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle |}{\underset{\displaystyle |}{Cr}}}}\overset{O\cdots H-O^*}{\underset{O\cdots H}{}} \right]^= \xrightarrow{k_4} CrO_2O^= + 2OH^- \qquad \text{rate-deter-mining}$$

$$CrO_2O^{*=} + H_2O^* \longrightarrow H_2CrO_2O_2^* \qquad \text{rapid}$$

$$H_2CrO_2O_2^* + 2OH^- \longrightarrow CrO_2O_2^{*=} + 2H_2O \qquad \text{rapid}$$

$$R = k_4 \frac{k'_1}{k'_{-1}} (CrO_4^=)(H_2O^*)$$
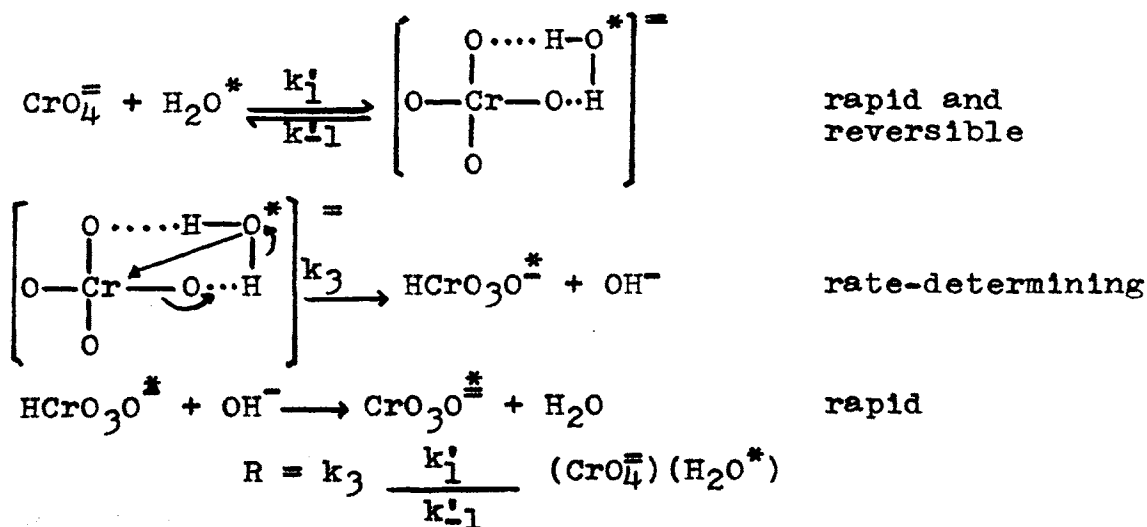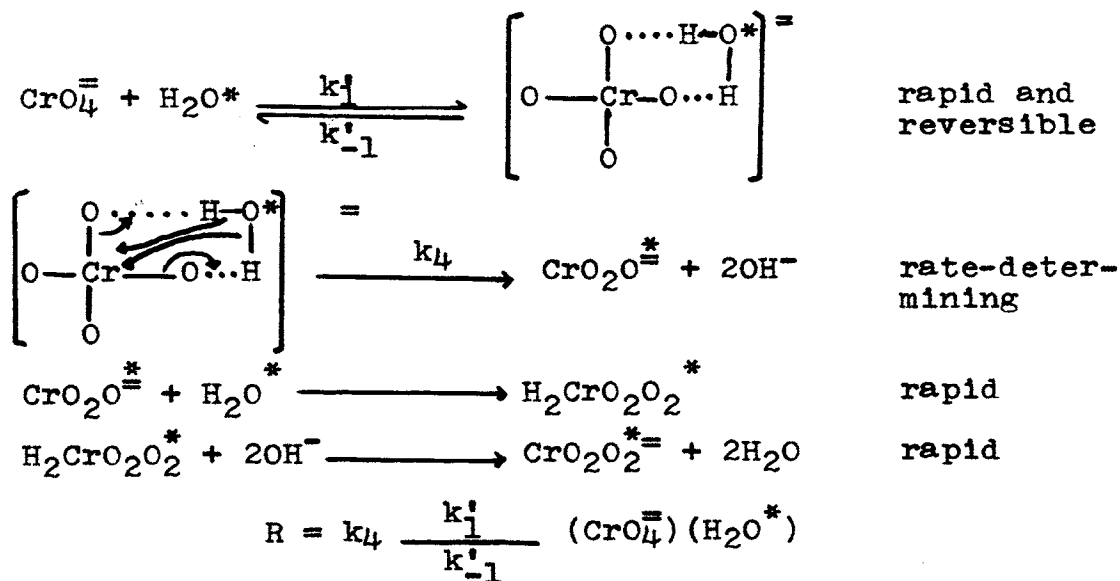
All of the above rate laws can be reduced to:

$$R = k(CrO_4^=)(H_2O)$$

or $\qquad R = k'(CrO_4^=)$

where

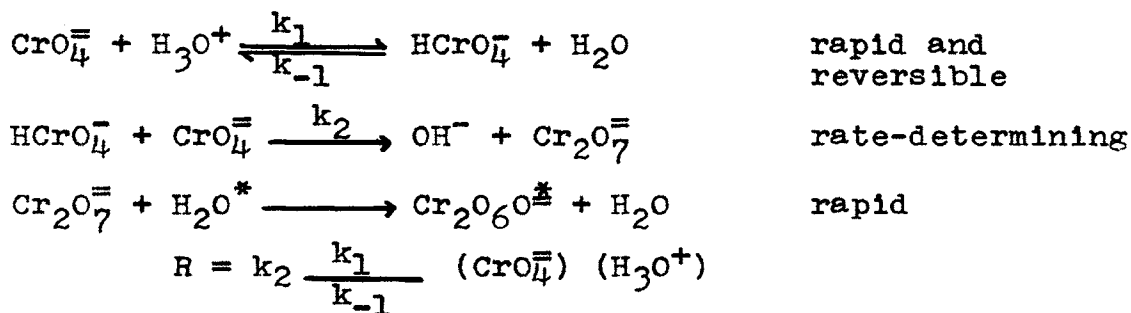$$k = k_2 \frac{k_1}{k_{-1}} \Gamma_1 \qquad \text{(for Mechanism I)}$$

$$k = k_3 \frac{k'_1}{k'_{-1}} \Gamma_2 \qquad \text{(for Mechanism II)}$$

and $\qquad k = k_4 \frac{k'_1}{k'_{-1}} \Gamma_3 \qquad \text{(for Mechanism III)}$

When the ionic strength of the reaction medium is held constant, the terms Γ_1, Γ_2, and Γ_3 which are functions of the activity coefficients of the reactants and the activated complex are assumed to be constant.

For solutions of pH values lower than 10, the exchange is acid dependent and there are two possible mechanisms to be formulated.

Mechanism IV:

$$CrO_4^= + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCrO_4^- + H_2O \qquad \text{rapid and reversible}$$

$$HCrO_4^- + CrO_4^= \xrightarrow{k_2} OH^- + Cr_2O_7^= \qquad \text{rate-determining}$$

$$Cr_2O_7^= + H_2O^* \longrightarrow Cr_2O_6O^{*=} + H_2O \qquad \text{rapid}$$

$$R = k_2 \frac{k_1}{k_{-1}} (CrO_4^=)(H_3O^+)$$

Mechanism V:

$$CrO_4^= + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCrO_4^- + H_2O \qquad \text{rapid and reversible}$$

$$HCrO_4^- + HCrO_4^- \xrightarrow{k_3} H_2O + Cr_2O_7^= \qquad \text{rate-determining}$$

$$Cr_2O_7^= + H_2O^* \longrightarrow H_2Cr_2O_7O^* \qquad \text{rapid}$$

$$H_2Cr_2O_7O^* \longrightarrow H_2O + Cr_2O_6O^{*=} \qquad \text{rapid}$$

$$R = k_3 \frac{k_1}{k_{-1}} (CrO_4^=)(HCrO_4^-)(H_3O^+)$$
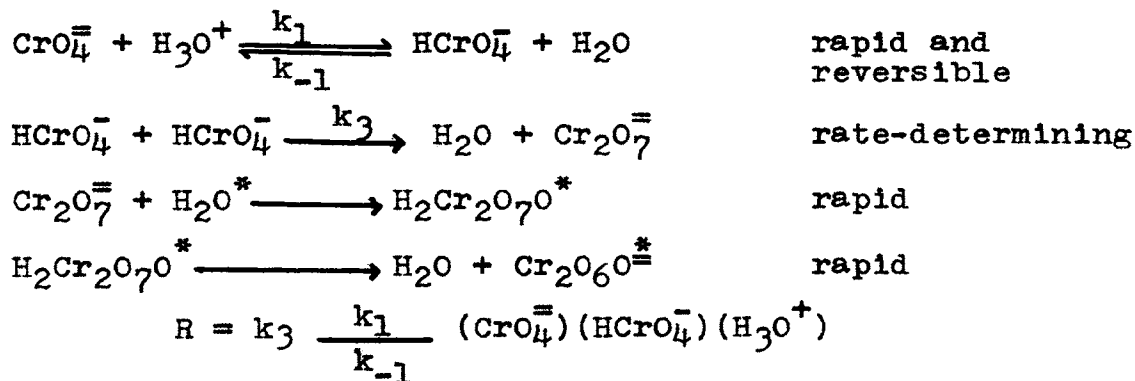
These two rate laws can be expressed by:

$$R = k_2'(H_3O^+)(CrO_4^=)^2 + k_3'(H_3O^+)(HCrO_4^-)(CrO_4^=)$$

$$\text{where} \quad k_2' = k_2 \frac{k_1}{k_{-1}} \Gamma_1$$

$$k_3' = k_3 \frac{k_1}{k_{-1}} \Gamma_2$$

Γ_1 and Γ_2 are assumed to be constant when the ionic strength of the reaction medium is held constant.

B. Rate Law and Evaluation of the Reaction Constants

1. Rate law:

From the proposed mechanisms, the rate of the oxygen exchange between the chromate ion and solvent water can be expressed by:

$$R = k_1(CrO_4^=)(H_2O) + k_2(HCrO_4^-)(CrO_4^=) + k_3(HCrO_4^-)^2 \qquad (1)$$

2. Evaluation of k_1, k_2, and k_3:

It is necessary to evaluate these specific rate constants k_1, k_2, and k_3. From the relationships among the $(HCrO_4^-)$, $(CrO_4^=)$, and $(Cr_2O_7^=)$ as:

$$K_1 = \frac{(HCrO_4^-)}{(H^+)(CrO_4^=)} \qquad (2)$$

$$K_2 = \frac{(Cr_2O_7^=)}{(HCrO_4^-)^2} \qquad (3)$$

the rate R can be expressed in terms of the concentrations of $CrO_4^=$ and H^+ only, this can be done by substituting (2) into (1):

$$R = k'(CrO_4^=) + k_2K_1(H^+)(CrO_4^=)^2 + k_3K_1^2(H^+)^2(CrO_4^=)^2 \qquad (4)$$

$$= (CrO_4^=)\left\{k_1' + k_2K_1(H^+)(CrO_4^=) + k_3K_1(H^+)^2(CrO_4^=)\right\}$$

Equation (4) may be used to evaluate k_1', k_2 and k_3. Since at high pH, the rate is nearly independent on the hydrogen ion concentration, i.e., the k_1' $(CrO_4^=)$ term will contribute the most in this equation to the rate, one may neglect the other terms, and k_1' is obtained.

The evaluation of k_2 and k_3 may be done from equation (4) by rearranging it; thus,

$$\frac{R - k_1'(CrO_4^=)}{(H^+)(CrO_4^=)^2} = k_2K_1 + k_3K_1^2(H^+) \qquad (5)$$

It is clear that by plotting the values of $\dfrac{R - k_1'(CrO_4^=)}{(H^+)(CrO_4^=)^2}$

vs. (H^+), the slope of the line will be the value of $k_3K_1^2$ and the intercept k_2K_1. The value of K_1 may be obtained by extrapolation from those data reported by other

workers: $K_1(\mu=0) = 3.16 \times 10^6 (21)$, $K_1(\mu=0.11) = 1.35 \times 10^6 (22)$, $K_1(\mu=4) = 7.0 \times 10^5 (13)$, and $K_1(\mu=3) = 7.94 \times 10^5 (13)$, and $K_1(\mu=3) = 7.94 \times 10^5 (5)$. From extrapolating data $K_1 = 1.26 \times 10^6$ at $\mu=1$. The plotting of

$$\frac{R - k_1'(CrO_4^=)}{(H^+)(CrO_4^=)^2}$$ vs. (H^+) is shown on Figure 7. The slope of the line is about 5.96×10^{15} and the intercept around 3×10^7. Then k_2 and k_3 are evaluated. The values for k_1' is 1.25×10^{-2} g-atom-oxygen l^{-1} hr^{-1} or 8.7×10^{-7} s^{-1}, k_2 is 1.67×10^{-3} M^{-1} s^{-1} and k_3 is 0.3 M^{-1} s^{-1}.

For the evaluation of k_{-2} and k_{-3} we have the following equations:

$$\frac{k_2}{k_{-2}} = \frac{(Cr_2O_7^=)(OH^-)}{(HCrO_4^-)(CrO_4^=)} = \frac{(HCrO_4^-)}{(H^+)(CrO_4^=)} \cdot \frac{(Cr_2O_7^=)}{(HCrO_4^-)^2} \cdot (H^+)(OH^-)$$

$$\text{or} \quad \frac{k_2}{k_{-2}} = K_1 K_2 K_w \tag{6}$$

$$\frac{k_3}{k_{-3}} = \frac{(Cr_2O_7^=)}{(HCrO_4^-)^2} = K_2 \tag{7}$$

$$\text{so,} \quad k_{-2} = \frac{k_2}{K_1 K_2 K_w} \tag{8}$$

$$k_{-3} = \frac{k_3}{k_2} \tag{9}$$

The k_{-2} and k_{-3} are so evaluated with the values of 1.35×10^3 M^{-1} s^{-1} and 3.06×10^{-3} M^{-1} s^{-1}, respectively.

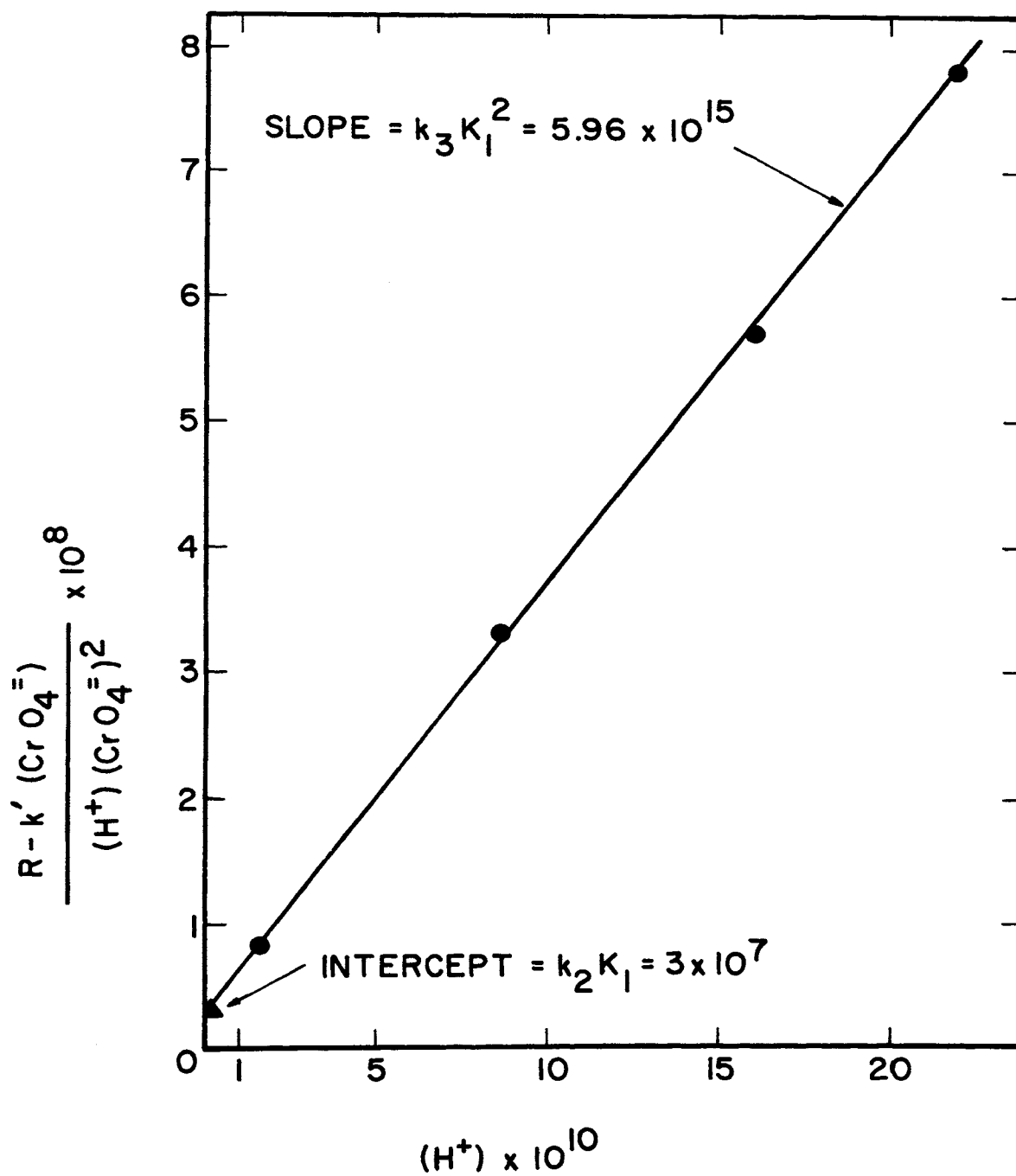C. Comparison of the data with those obtained from other Methods:

Figure 7. Determination of $k_3K_1^2$ and k_2K_1

Table VIII summarizes the rate constants for the process reported in this study along with the results obtained by other methods.

The slower rates were assumed to result when the solutions were free from adventitious impurities which might catalyze the exchange. Also, in this work the temperature is $30^{\circ}C$ instead of the $25^{\circ}C$ used by the other workers. The agreement of the results obtained by the variety of methods under markedly different conditions of concentration is remarkable.
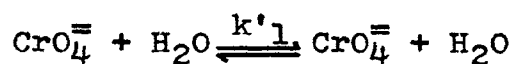
D. The Activation Energy and the Isotope Effect:

Many acid-catalyzed reactions are found to proceed faster in D_3O^+ than in H_3O^+[23][24],

$$D_3O^+ + CrO_4^= \rightleftharpoons DCrO_4^- + D_2O \qquad (10)$$

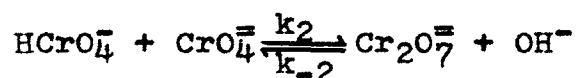$$H_3O^+ + CrO_4^= \rightleftharpoons HCrO_4^- + H_2O \qquad (11)$$
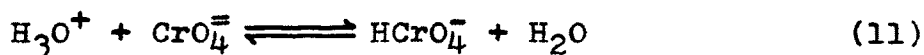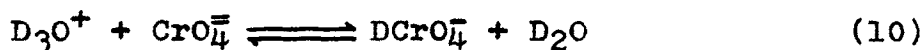
The position of the equilibrium in equation (10) may be expected to lie farther to the right than the position of the equilibrium in equation (11). That is, the net energy difference between the zero point energies of products and reactants in equation (10) is larger than the net energy difference between products and reactants in (11). The deuterium isotope effect for the exchange of oxygen between chromate ion and water gave $R_D/R_H =$ 1.64 at pH 7.20, since chromic acid is a strong acid we should expect the large isotope effect which was observed.
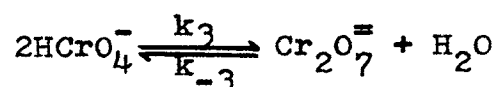
Table VIII. Comparison of Rate Constants Obtained
in This Study with Values Derived from
Other Methods

$$CrO_4^= + H_2O \xrightleftharpoons{k'_1} CrO_4^= + H_2O$$

$k'_1(s^{-1})$	Ref.	Temp.(^{o}C)
8.7×10^{-7}	This work	30
7.0×10^{-7}	(13)	25
1.2×10^{-5}	(12)	25

$$HCrO_4^- + CrO_4^= \xrightleftharpoons[k_{-2}]{k_2} Cr_2O_7^= + OH^-$$

$k_2(M^{-1}s^{-1})$	$k_{-2}(M^{-1}s^{-1})$	Ref.	Temp.(^{o}C)
1.67×10^{-3}	1.35×10^3	This work	30
2.40×10^{-3}	2.10×10^3	(13)	25
8.80×10^{-4}	4.60×10^2	(8)	25

$$2HCrO_4^- \xrightleftharpoons[k_{-3}]{k_3} Cr_2O_7^= + H_2O$$

| $k_3(M^{-1}s^{-1})$	$k_{-3}(M^{-1}s^{-1})$	Ref.	Temp.(^{o}C)
3×10^{-1}	3.06×10^{-3}	This work	30
1.3	1.40×10^{-4}	(13)	25
1.8	4.90×10^{-4}	(9)	23

For the solutions of pH higher than 8, the isotope effect R_D/R_H is less than 1. This can be explained by mechanisms I, II, and III, since all of these mechanisms involve a bond rupture between H and O in the rate-determining step.

V. CONCLUSION

In the pH region where the oxygen exchange between chromate ion and water was studied, namely from a pH of 11.50 to a pH of 7.20, the exchange has the rate law

$$R = k_1(CrO_4^=)(H_2O) + k_2(HCrO_4^-)(CrO_4^=) + k_3(HCrO_4^-)^2$$

From the experimental results, we may propose that the slow pH-independent exchange observed in the region of pH greater than 10 is consistent with the process:

$$CrO_4^= + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrO_4^= + H_2O$$
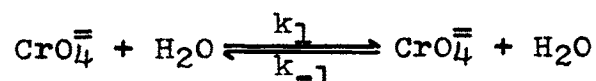
The near first-order hydrogen ion dependence and second-order chromate ion concentration dependence in the pH range 8--10 may be explained in terms of:

$$HCrO_4^- + CrO_4^= \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cr_2O_7^= + OH^-$$

For the exchange at pH lower than 8, the increasing dependence on hydrogen ion concentration may be due to a contribution by the following process:

$$2HCrO_4^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Cr_2O_7^= + H_2O$$
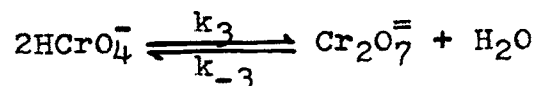
For the pH below 6, the exchange goes too fast to measure by the present method; the flow technique may be used to advantage.

The exchange path suggested in the region of below pH 8 is probably the two dimerization equilibria, $HCrO_4^- + CrO_4^= \rightleftharpoons Cr_2O_7^= + OH^-$ and $2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$. The exchange path in the region of above pH 10 is best shown

by mechanism II, and the exchange path in the region of pH from 7.2 to 10 by mechanism IV and V.

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