# THE KINETICS OF THE OXIDATION-REDUCTION REACTION BETWEEN MANGANATE AND PERRUTHENATE ANIONS IN AQUEOUS ALKALI

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# ABSTRACT

## THE KINETICS OF THE OXIDATION-REDUCTION REACTION BETWEEN MANGANATE AND PERRUTHENATE ANIONS IN AQUEOUS ALKALI

by E. Victor Luoma

The kinetics of the oxidation-reduction reaction between manganate and perruthenate anions was studied at 20.0°C in alkaline aqueous solution. The rate was determined spectrophotometrically. The reaction is first order with respect to each ion and has a measurable equilibrium constant. Rate constants ranged between 500-1500 $\underline{M}^{-1}$sec.$^{-1}$, depending on experimental conditions. The rate is a function of the cation present, and increases with an increase in the size or concentration of the cation. The temperature dependence of the reaction was studied and $\underline{E}_a$ = 7.65 kcal/mole, $\Delta S^{\ddagger}$ = -10.7 e.u., and $\Delta G^{\ddagger}$ = 10.2 kcal/mole were obtained. The equilibrium constant is 4.32 ± 0.25 at 20.0°C. The temperature dependence of the equilibirum constant was determined and $\underline{\Delta H^0}$ = 3.95 kcal/mole, $\underline{\Delta G^0}$ = -0.85 kcal/mole, and $\underline{\Delta S^0}$ = -10.6 e.u. were calculated. The results of the rate study are compared with the theory of R. A. Marcus.

A preliminary study of the electron exchange reaction between ruthenate and perruthenate at 0°C in 0.10 $\underline{M}$ sodium hydroxide solution was made. The exchange was too fast to measure and a minimum value of $\sim 10^4$ $\underline{M}^{-1}$sec.$^{-1}$ for a second order rate constant was estimated.

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By

E. Victor Luoma

A THESIS

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# DEDICATION

This work is dedicated to my father, Ernie S. Luoma, who taught me the value of diligence and education.

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# I. INTRODUCTION

In recent years there has been much kinetic and mechanistic work in the field of inorganic chemistry (1). Although the bulk of this work has been in the area of ligand substitution reactions, there has been considerable work in the field of electron transfer reactions (2,3,4,5,6). A few of the reactions studied have been of the type where simple electron exchange is a possible mechanism, such as the case of the manganate-permanganate electron transfer reaction studied by Sheppard and Wahl (7).

$$MnO_4^- + \overset{*}{Mn}O_4^{2-} \rightleftharpoons MnO_4^{2-} + \overset{*}{Mn}O_4^-$$

Symons (33) has shown that there is no interpenetration of the first coordination spheres and hence the reaction must proceed <u>via</u> an "outer-sphere" mechanism.

This investigation originally started as a study of the electron transfer reaction between ruthenate and perruthenate, which was chosen because its close resemblance to manganate-permanganate might provide further data for elucidating the mechanism of electron transfer reactions in complexes with inert first coordination spheres. The reaction proved to be too fast to measure and only a minimum value for the rate constant was determined. The ruthenate-perruthenate work is discussed in the Appendix.

It was decided to investigate the oxidation of manganate by perruthenate, since such a study might give additional

kinetic information involving the species discussed above.

$$RuO_4^{-} + MnO_4^{2-} \rightleftharpoons RuO_4^{2-} + MnO_4^{-}$$

In this system there was no need to use tracers since there is a net chemical change. All four anions absorb strongly in the visible region and spectrophotometry could be used to determine the initial concentrations of the reactants and to follow the course of the reaction.

The reaction turned out to be an equilibrium process in which $\underline{K_{eq}}$ was not very large (~4) and thus it was possible to determine the free energy, enthalpy, and entropy of reaction in addition to the usual kinetic constants. The study of the reaction was complicated by competing reactions which will be discussed later. The competing reactions made the determination of the equilibrium constant for the perruthenate-manganate reaction difficult and restricted the kinetic study to alkaline media between 0.10 $\underline{M}$ and 1.0 $\underline{M}$ hydroxide.

# II. HISTORICAL

Electron transfer kinetics has become an active area of research since radioisotopes became readily available. It has only been since about 1950 that sufficient experimental work has been published to allow attempts at quantitative explanations of the factors which govern the rates of electron transfer. A number of systems have been studied and the effects of acids, bases, anions, cations, heavy water, alcohol, and other agents have been examined (2,3,4,5). From these studies, it now appears that there are three possible paths for effecting transfer of electrons (6). In any given reaction one or more of these paths may be operative.

In some systems it appears that bridged species are formed in which the reactants are joined together in the transition state by an ion or group. Another process involves the actual transfer of an atom, radical, or molecule. These two processes are referred to as "strong over-lap mechanisms". In some cases it is possible to distinguish between them but more frequently there is an ambiguity. In either case, however, the strong over-lap mechanisms are considered to involve the first coordination sphere of the reactants directly.

In systems where the ligands are inert to substitution a "weak over-lap mechanism" has been proposed. The activated complex is designated as an outer-sphere complex but its structure is difficult to ascertain. In such a mechanism the transfer of the electron is considered to be a quantum mechanical, barrier penetration. Electron transfer in systems considered to be examples of the weak-overlap mechanism is fast and only a few have been studied. The example of prime interest in this study is manganate-permanganate in which the rate of exchange was found to be on the order of 1000 $\underline{M}^{-1}sec^{-1}$ at 0°C and to have first-order dependence on each reactant: a second-order reaction (7). The rate was also found to depend on both the cation concentration and nature.

There are several theoretical approaches to the weak-overlap mechanism. The work of R. A. Marcus (12,13,14,15) has achieved the widest acceptance and derives rate expressions with no adjustable parameters. The R. A. Marcus model will be applied to this investigation in the following section. Other theories include one by R. J. Marcus, Zwolinski, and Eyring (11) in which an experimental system is necessary for the calibration of parameters. Hush (8) has derived an "adiabatic" theory which gives essentially the same results as those of the R. A. Marcus model. The approach by Laidler (9,10) in his "non-adiabatic" theory is similar to that of Marcus, Zwolinski, and Eyring. The various theories have recently been reviewed by R. A. Marcus (16) and there is a discussion of some of the recent work applied to theory by Strehlow (17). In all of the theories a knowledge of the transition state is required and is not generally obtainable from rate studies alone.

# III. THEORETICAL

## A. The Rate Law

In simple systems determination of the rate law for a chemical reaction generally involves mixing of the reactants and following the concentrations *versus* time at constant temperature. The data obtained are then fitted to various rate expressions of the type:

$$\frac{dC_A}{dt} = k\ C_A^{\alpha} C_B^{\beta} C_C^{\gamma} \cdots\cdots \qquad [1]$$

where *k* is the specific reaction rate constant; $\alpha$, $\beta$, $\gamma$ ··· are often integers; and $C_A$, $C_B$, $C_C$···· are the concentrations of the chemical species *A*, *B*, *C* ···· present in the reacting system at time *t*. Various graphical and mathematical methods are available for determining the values of $\alpha$, $\beta$, $\gamma$ ···· which will give a constant value for *k* (18).

If the system under study is more complex, i.e., has opposing, concurrent, or consecutive reactions, then the mathematics becomes such that general methods of solution are impractical or impossible. In this case the data are fitted to equations for the various possible rate laws to determine which one is obeyed. Additional information about the reaction in question such as its stoichiometry and the concentrations at equilibrium can help narrow the search for the correct rate law.

In this investigation the reaction was determined to have an observable equilibrium constant and the stoichiometric equation was found to be:

$$RuO_4^- + MnO_4^{2-} \rightleftharpoons RuO_4^{2-} + MnO_4^- .$$

Data were successfully fitted to the rate law for second-order, opposing reaction. Such a rate law is developed by Benson (19) for the general case represented by the equation:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D .$$

The rate law is:

$$\frac{[dA]}{dt} = - k_1[A][B] + k_2[C][D] \qquad [2]$$

or by letting $A = A_0 - x$ :

$$\frac{dx}{dt} = k_1(A_0 - x)(B_0 - x) - k_2(C_0 + x)(D_0 + x) . \qquad [3]$$

The solution has the form:

$$\ln \frac{x + (\beta - q^{1/2})/2\gamma}{x + (\beta + q^{1/2})/2\gamma} = tq^{1/2} + \theta \qquad [4]$$

where: $\theta = \dfrac{\beta - q^{1/2}}{\beta + q^{1/2}}$

$q = k_1^2(A_0 - B_0)^2 + k_2^2(C_0 - D_0)^2$
$\quad + 2k_1k_2[(A_0 + B_0)(C_0 + D_0) + 2A_0B_0 + 2C_0D_0]$

$\beta = - (k_1A_0 + k_1B_0 + k_2C_0 + k_2D_0)$

$\gamma = k_1 + k_2$

$t$ = time.

With a knowledge of the equilibrium constant, K, for the reaction it is possible to factor out $\underline{k_1}$ from $\underline{q}^{1/2}$, $\underline{\beta}$, and $\underline{\gamma}$ so that there are no rate constants in the log term. The equation then becomes:

$$\ln \frac{x + (\text{Beta} - Q^{1/2})/\text{gamma}}{x + (\text{Beta} + Q^{1/2})/\text{gamma}} = k_1 t Q^{1/2} + \theta \qquad [5]$$

where:

$$\theta = \ln \frac{\text{Beta} - Q^{1/2}}{\text{Beta} + Q^{1/2}}$$

$$Q = (A_0 - B_0)^2 + \frac{1}{K^2}(C_0 + C_0)^2 + \frac{2}{K}[(A_0 + B_0)$$

$$(C_0 + D_0) + 2A_0B_0 + 2C_0D_0]$$

$$\text{Beta} = -[A_0 + B_0 + \frac{1}{K}(C_0 + D_0)]$$

$$\text{Gamma} = 2(1 - \frac{1}{K})$$

K = equilibrium constant.

A plot of the log term *versus* time for a given reaction gives a slope of $\underline{k_1Q}^{1/2}$ from which $\underline{k_1}$ is readily determined. Note that the term

$$(\text{Beta} + Q^{1/2})/\text{gamma}$$

in the denominator of the log term is the equilibrium concentration of $\underline{x}$.

## B. Theoretical Prediction of the Rate Constant

The equations derived from the model due to R. A. Marcus will be used for comparison with the experimental data of this investigation. Marcus' theory is applicable to systems in which there is only small orbital overlap between the reactants in the activated complex. Such is considered to be the case when the first coordination sphere of the reactants is non-labile and when the ions are only weakly solvated. The first condition of non-lability is probably met in the manganate-perruthenate system but there is a question about hydroxide ion association which will be discussed later.

The equations given below summarize the results of the Marcus theory and are taken from Rasmussen and Brubaker (20). A detailed development of the theory may be found in the original papers (12,13,14,15). The factor $\exp[-\kappa r]$ used by Rasmussen and Brubaker to correct for ionic strength will be used here, although Marcus has recently published the ionic strength correction in a somewhat different form (13).

$$k_r = Z \exp[-\Delta G^{\ddagger}/RT] \qquad [6]$$

$$\Delta G^{\ddagger} = \frac{e_1 e_2}{D_s r} \exp[-\kappa r] + m^2\lambda \qquad [7]$$

where:

$k_r$ = rate constant

$Z$ = collision number in solution equals about $10^{11}$

$T$ = absolute temperature ($^0$K)

$D_s$ = dielectric constant of the solvent

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

$e_1 e_2$ = charges on the reactants

$r$ = distance of closest approach of the reactants

$\kappa$ = "Debye-Hückel kappa" equal to $(5.03 \times 10^9)\sqrt{\mu/D_s T}$

$\mu$ = ionic strength

$$m = [-\frac{\Delta G^0 + w - w^*}{2\lambda}] - \frac{1}{2} \text{ (ref. 15)} \qquad [8]$$

$$\lambda = \lambda_0 + \lambda_i$$

$$\lambda_0 = (\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r})(\frac{1}{\eta^2} - \frac{1}{D_s})(\Delta e)^2 \qquad [9]$$

$$\lambda_i = \sum_j \frac{K_j K_j^P}{K_j + K_j^P} (\Delta q_j^0)^2 \qquad [10]$$

where:

$\Delta G^0$ = free energy of reaction

$w, w^*$ = work of bringing together reactants and separating products.

$r$ = $a_1 + a_2$

$\eta$ = refractive index of the solvent

$\Delta e$ = amount of charge transferred as a result of the reaction.

$K_j, K_j^P$ = force constants of the $j^{th}$ vibrational coordinate for a species as reactant and product respectively.

$\Delta q_j^0$ = change in the bond distance in the inner coordination sphere of each reactant.

$\lambda_0$ = "lambda outer"; contribution to $\lambda$ of surroundings of activated complex.

$\lambda_i$ = "lambda inner"; contribution to $\lambda$ of changes in the first coordination sphere.

To determine $\underline{\lambda_i}$, the summation is over the $\underline{j}$ normal modes of each reactant and over all bonds involved in a particular mode. In a regular tetrahedron only one of the $\underline{j}$ normal coordinates involves significant deformation on going from reactant to product (21). This corresponds most closely to bond stretching. To estimate $\underline{\lambda_i}$ , the equilibrium bond length change, $\underline{\Delta q^0}$, and the force constant of the bond in each reactant and product must be determined.

The Mn-O distance in potassium permanganate has been determined to be 1.59Å (22). Sheppard and Wahl have estimated the Mn-O distance in potassium manganate to be 1.60-1.61Å (7). The value 1.605Å will be used here, giving a $\underline{\Delta q^0}$ = 0.015Å for the manganese contribution to $\underline{\lambda_i}$ . Silverman and Levy (23) have determined the Ru-O distance in potassium perruthenate to be 1.79Å. Using the relationship given by Pauling (24):

$$\frac{r_Z}{r_{Z+1}} = \left(\frac{Z}{Z+1}\right)^{-\frac{2}{n-1}} \qquad [11]$$

where n ≈ 10 for ruthenium, a value of 1.804Å was calculated for the Ru-O distance in potassium ruthenate. For the ruthenium contribution to $\underline{\lambda_i}$ , $\underline{\Delta q^0}$ = 0.014Å.

The force constants are estimated using an empirical rule of Badger (25):

$$(C/K)^{1/3} = r_e - d_{ij} \qquad [12]$$

where: $C^{1/3}$ = an empirical constant equal to 0.500 for a bond between first and third row atoms and 0.490 between first and fourth row atoms.

$d_{ij}$ = an empirical constant equal to 1.06 for a bond between first and third row atoms and 1.18 between first and fourth row atoms

$r_e$ = equilibrium bond length in Angstroms

K = force constant of bond in megadynes per centimeter.

By use of the above rule, the force constants are:

| | |
|---|---|
| Mn(VI) - O | $K = 7.97 \times 10^5$ dynes/cm. |
| Mn(VII) - O | $K = 8.39 \times 10^5$ dynes/cm. |
| Ru(VI) - O | $K = 4.85 \times 10^5$ dynes/cm. |
| Ru(VII) - O | $K = 5.19 \times 10^5$ dynes/cm. |

Substituting into the equation for $\lambda_i$ yields:

$$\lambda_i = \lambda_i(\mathrm{Mn}) + \lambda_i(\mathrm{Ru})$$

$$\lambda_i = 1.41 \times 10^{-14} \text{ ergs.} \qquad [13]$$

To calculate $\lambda_0$, the value of one-half the Mn-Mn and Ru-Ru distances in potassium manganate (22) and potassium perruthenate (23) will be used for $a_1$ and $a_2$, respectively. This makes $a_1 = 2.955\text{Å}$ and $a_2 = 2.805\text{Å}$. At 20°C, $D_s = 80.4$ and $\eta = 1.33$ for water. Substitution of these values gives:

$$\lambda_0 = 2.22 \times 10^{-12} \text{ ergs} \qquad [14]$$

$$\lambda = 2.23 \times 10^{-12} \text{ ergs.} \qquad [15]$$

It is easily seen that "lambda inner" makes very little contribution to the total, which is not surprising in view of the very small changes in bond distances which accompany the transfer of the electron.

To calculate $m$ from equation [8], $\Delta G^0 = -5.85 \times 10^{-14}$ ergs/molecule determined from the equilibrium constant for the reaction (see Results section of this thesis) is used. This makes $m = -0.487$. For $e_1e_2$ $(2)(4.8 \times 10^{-10})^2$ e.s.u. is used. Substitution of the appropriate values into equation [7] gives:

$$\Delta G^{\ddagger} = 8.21 \text{ kcal/mole} \qquad [16]$$

$$k_r = 7.8 \times 10^4\ \underline{M}^{-1}\text{sec}^{-1}. \qquad [17]$$

This value for the rate constant is for reaction in a solution of ionic strength $\mu = 0.20$ and for the reactants approaching as closely together as they might in a crystal. If a water molecule intervenes between the two anions, the value of $r$ increases to about 10.1Å. Recalculating the above values we find:

$$\Delta G^{\ddagger} = 4.31 \text{ kcal mole} \qquad [18]$$

$$k_r = 6.2 \times 10^7\ \underline{M}^{-1}\text{sec.}^{-1} \qquad [19]$$

These two values for $k_r$ will be compared to the experimental value in the Discussion section of this thesis.

# IV. EXPERIMENTAL

## A. Preparation of Reagents

Reagent grade materials were used except for lithium hydroxide from the Amend Drug and Chemical Company, cesium iodide from the Fairmount Chemical Company, and rubidium sulfate and ruthenium metal from K and K Laboratories, Incorporated. Low carbonate ($< 0.35\%$) sodium hydroxide was used. The water used to prepare solutions was distilled and then passed through a mixed-resin ion-exchange column to give a metal ion content of less than one part per million, determined by conductance. Contamination of the water by organic matter from the resin was reduced by discarding the first quantity of water passed through the resin. Glassware was washed thoroughly with hot bleach ("Clorox"), rinsed with distilled water, and air dried.

Stock solutions of lithium, sodium, and potassium hydroxides were prepared by diluting concentrated solutions after decantation from residual solids. Hydroxide concentrations were determined by titration to the acid side of methyl orange to include alkali-metal carbonate content, since it was anticipated that the reactions would be dependent upon cation concentration. Stock solutions of sodium phosphate, sodium sulfate, sodium perchlorate, sodium nitrate, rubidium sulfate, and cesium sulfate were prepared by weighing the reagent, after it had been dried, and diluting to a known volume.

Cesium sulfate was prepared by adding dilute sulfuric acid to cesium iodide and evaporating on a hot plate until sulfuric acid fumes appeared to remove the iodine which had formed. The resulting mass was heated to ~600°C to remove the excess sulfuric acid. More sulfuric acid was added after the mass had cooled and it was heated again to ~1000°C.

A stock solution of Ru(III) was prepared by fusion of ruthenium metal with potassium hydroxide and potassium nitrate at 600°C (26). The fused mass was dissolved in water and acidified with sulfuric acid. The solution was evaporated to sulfuric acid fumes. During the evaporation several portions of hydrochloric acid were added to destroy excess nitrate. The resulting solution was diluted with water and sulfuric acid to make a Ru(III) stock in 3 M $H_2SO_4$. Perruthenate solutions were prepared by oxidizing Ru(III) with sodium bismuthate in hot 3 M $H_2SO_4$ (27). The resulting ruthenium tetroxide was swept from the solution with a stream of air and carried into a solution of hydroxide of known concentration (~1 M) where the ruthenium tetroxide decomposed to give perruthenate. A measured volume of this solution was then diluted to give the desired alkalinity. The perruthenate concentration was controlled approximately by the amount of Ru(III) stock added to the still. Perruthenate solutions containing sodium perchlorate, sodium sulfate, etc. in addition to hydroxide were prepared by adding a measured volume of the appropriate stock solution before diluting the alkaline perruthenate to final volume. Perruthenate solutions were stored in an ice bath. Perruthenate solutions in high hydroxide concentrations ($> 0.6$ M), had to be used the same day as prepared. For lower concentrations of hydroxide, the solutions could be stored for up to a week.

Three different procedures were used to prepare manganate solutions. In the first manganese dioxide was fused in sodium hydroxide and was subsequently diluted to give a manganate stock in 3 M $OH^-$. In the second method potassium permanganate was decomposed in $> 3$ M $OH^-$ and diluted to the required hydroxide concentration. Even though this second method contaminated the sodium hydroxide solutions to the extent of about 0.1% with potassium ion, the same rates were obtained for these solutions as for those prepared by the first method. Neither of these two methods is suitable for the lithium hydroxide solutions, because lithium ion accelerated the decomposition of manganate solutions. In the third method of manganate preparation potassium permanganate was dissolved in hot, concentrated potassium hydroxide. After it was cooled, the resulting potassium manganate was filtered off, washed with cold 1 M potassium hydroxide, and air dried. Manganate solutions were then prepared by adding a few crystals of the potassium manganate to water with the desired hydroxide and cation concentrations. This last procedure was used for all experiments with solutions containing lithium hydroxide and for about half of those with sodium and potassium hydroxide. All manganate solutions were stored in an ice bath and had to be used within one day after preparation and usually were used within about four hours.

## B. Analytical Methods

Spectrophotometry was used to determine the initial concentrations of reactants and to follow the course of the reaction. Molar absorptivities, $\underline{\varepsilon}$ , reported in the literature for the four species, ruthenate, perruthenate, manganate, and permanganate, are somewhat contradictory (27,28,29,30, 31,32,35,43,44). Therefore, absorptivities were determined for each anion at several wavelengths.

Solutions of known ruthenate concentration were prepared by oxidizing ruthenium metal to perruthenate with hypochlorite in 1 $\underline{M}$ NaOH and then decomposing the perruthenate to ruthenate in 5-8 $\underline{M}$ NaOH. The absorbancies at 385 and 465 mμ were measured periodically during the conversion until there was no further change, i.e., until the ratio of $\underline{\varepsilon}_{465}/\underline{\varepsilon}_{385}$ had reached a maximum. The molar absorptivities at several wavelengths were then determined by means of a Beckman, Model DU, spectrophotometer, and are listed in Table I. The only maximum in the visible region for ruthenate is at 465 mμ. Ruthenate of known concentration was then oxidized to perruthenate with 0.05 $\underline{M}$ NaClO in 1 $\underline{M}$ NaOH to determine the molar absorptivities for perruthenate. The results are given in Table I and agree well

Table I. Molar absorptivities at 20$^0$C.

| Wavelength | | $\varepsilon_{RuO_4^-}$ | $\varepsilon_{RuO_4^{2-}}$ | $\varepsilon_{MnO_4^-}$ | $\varepsilon_{MnO_4^{2-}}$ |
|---|---|---|---|---|---|
| cm$^{-1}$ | mμ | | | | |
| 26,000 | 385 | 2150 | 840 | 340 | 1200 |
| 24,110 | 414.7 | 1075 | 1075 | 40 | 1080 |
| 21,500 | 465 | 260 | 1740 | 395 | 760 |
| 21,150 | 472.8 | 250 | 1720 | 560 | 560 |
| 19,700 | 507 | 170 | 1120 | 1805 | 240 |
| 19,000 | 526 | 120 | 610 | 2395 | 420 |
| 16,500 | 608 | 70 | 30 | 200 | 1570 |

with those of Larsen and Ross (27). The ratio $\underline{\varepsilon}_{465}/\underline{\varepsilon}_{385}$ was found to be 0.121 for solutions of perruthenate prepared by the above method. This same ratio was also found for fresh samples of perruthenate prepared by the decomposition of ruthenium tetroxide in alkali of 1 $\underline{M}$ or lower. The ratio, 0.121, agrees with that reported by Nowogrocki and Tridot (28). Visible spectra given elsewhere (27,28,29,30) were confirmed. Solutions of both ruthenate and perruthenate were found to obey Beer's law, at all wavelengths, up to the highest concentrations studied ($5 \times 10^{-4}$ $\underline{M}$). Dilution of a solution containing perruthenate from one concentration of alkali to another was found to cause a change in the relative proportion of perruthenate and ruthenate present and, so, concentrations had to be determined after dilution.

Standard solutions of permanganate were prepared by dissolving electrolytic manganese metal in dilute nitric acid to give manganese(II), and subsequent oxidation to permanganate with periodate (31). The molar absorptivities at several wavelengths are given in Table I. Manganate solutions were prepared by decomposing permanganate in $> 5$ $\underline{M}$ $OH^-$ and subsequently diluting the solutions to 1 $\underline{M}$ $OH^-$. It was found that dilution had to be performed carefully to prevent disproportionation of the manganate. By use of ice cold 0.1 $\underline{M}$ $OH^-$ as the diluent and by rapid stirring, the disproportionation reaction was prevented. The concentrations of manganese in these solutions were determined spectrophotometrically after acidification of measured volumes with phosphoric acid and periodate oxidation to permanganate. The molar absorptivities for manganate are given in Table I. Figure 1 shows the visible spectrum for manganate. In addition to the maximum at 606 mμ ($\underline{\varepsilon}$ = 1570), there are two others in the visible region at 438 and 353 mμ with molar absorptivities of 1270 and 1610, respectively. These values differ somewhat from those found (1260 and 1530) by Bennet and Holmes (32). The latter values could be duplicated, if small amounts of permanganate were present in the manganate solutions. Solutions of manganate and permanganate were found to obey Beer's law at all wavelengths up to the highest concentrations studied ($5 \times 10^{-4}$ $\underline{M}$). All of the molar absorptivities were determined at 20°C.

## C. Procedure

Samples of each reactant were warmed to 20°C and the absorbancies were measured at 385 and 465 mμ for the perruthenate stock and at 507 and 608 mμ for the manganate stock to obtain the concentrations of perruthenate, ruthenate, permanganate, and manganate ions. The absorbancy of the perruthenate stock was also measured at 507 or 608 mμ, depending on which wavelength was to be used to measure the kinetics. The absorbancies were measured in the reaction cell with a Cary, Model 14, spectrophotometer which was also used to monitor the reaction.

The pyrex reaction cell was cylindrical and had a capacity of 65 ml and a 10.2-cm light path. The opening of

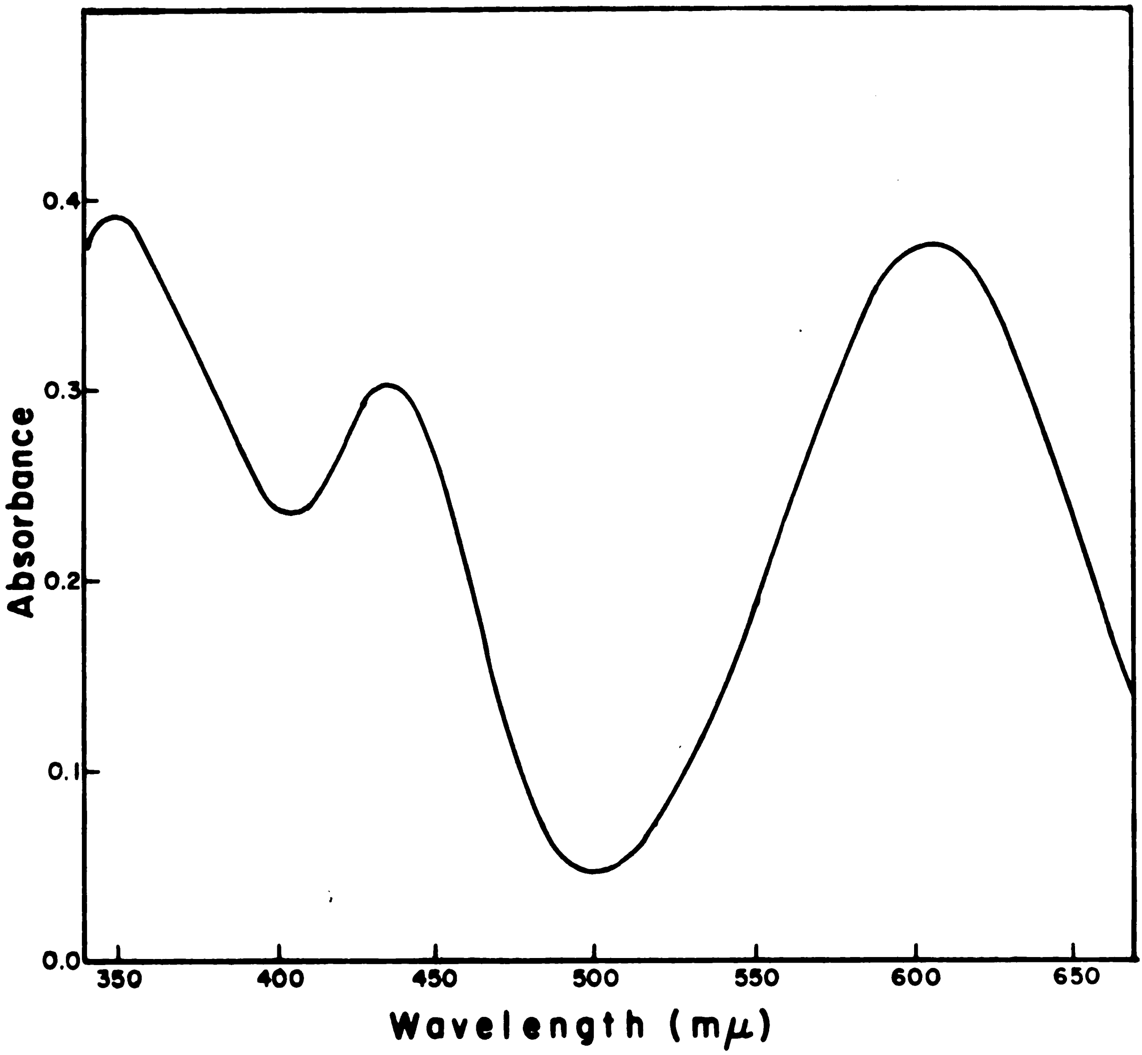

Figure 1. Visible absorption spectrum of $2.39 \times 10^{-4}$ M $MnO_4^{2-}$ in 1.0 M NaOH.

the cell was approximately 2-cm in diameter and was formed by a glass tube about 5-cm long to permit rapid filling of the cell. A special cover with an opening was built for the spectrophotometer cell-compartment which permitted the cell to be filled while the cell and cover were in position.

For each rate determination, a measured volume of each stock solution was pipetted into a separate electrolytic beaker. The beakers were covered with watch glasses and placed in a constant temperature bath. The bath temperature was measured with a precision thermometer, which had been compared with a calibrated Beckmann thermometer (calibrated against a platinum resistance thermometer). The bath temperature was held to within ± 0.01°C. Water from the bath was circulated by a centrifugal pump through the water-jacket of the spectrophotometer cell-compartment.

The reaction cell was washed with deionized water, dried by suction, and placed in the thermostatted cell-compartment. When the cell had come to bath temperature, the two reactants were removed from the bath, mixed by being poured back and forth from one beaker to the other, and then were transferred quickly to the cell through the opening in the cover. The opening in the cover was then closed and the instrument turned on to record the absorbancy <u>versus</u> time at a fixed wavelength. The temperature of solutions, after the reaction was complete, had not changed from the bath temperature.

The extent of reaction was determined by use of the molar absorptivities given in Table I. Because of the competing reaction, the absorptivities of only a few solutions could be measured, at more than one wavelength, after the reaction was completed. This was done to determine the validity of the use of net absorbancy change as a measure of the reaction variable $\underline{x}$ (equation [3], Section III-A). The validity of that assumption was upheld when it could be checked and the additional assumption was made that the absorbancy change at a single wavelength could be used in all experiments. A few reactions were run at 608 mμ to observe the disappearance of reactant. Duplicate reactions were repeated at 507 mμ to observe the appearance of product. The same values for the rate constant were obtained at both wavelengths. The bulk of the reactions were then carried out at 507 mμ, because the absorbancy change for a given set of reactants is about 75% greater at 507 mμ than 608 mμ. Since the quantity desired was the slope of the line obtained from the function:

$$\ln \frac{x + (\text{Beta} - Q^{1/2})/\text{gamma}}{x + (\text{Beta} + Q^{1/2})/\text{gamma}} = k_1 t Q^{1/2} + \theta$$

zero time was taken at the first absorbance reading of a given experiment. The rate constants were determined by a least-squares analysis of the data performed by a Control Data-3600 computer.

## D. Competing Reactions

In addition to the reaction

$$RuO_4^{-} + MnO_4^{2-} = RuO_4^{2-} + MnO_4^{-} \qquad [20]$$

there are at least five competing reactions which take place in alkaline solutions of manganate, permanganate, ruthenate, and perruthenate.

The decomposition of perruthenate at 25°C has been studied by Carrington and Symons (34). The reaction

$$4\ RuO_4^{-} + 4\ OH^{-} \longrightarrow 4\ RuO_4^{2-} + 2\ H_2O + O_2 \qquad [21]$$

was found to follow the rate law

$$\frac{dx}{dt} = k[RuO_4^{-}]^2[OH^{-}]^3 \qquad [22]$$

where: $k = 7.1 \times 10^{-2}\ \underline{M}^{-4}sec.^{-1}$

except for the first 10-20% of the reaction where the rate appears to be proportional to $[RuO_4^{-}]^3$. A measurement of the rate of reaction [21] at lower $OH^{-}$ concentrations (0.02 - 1.0 $\underline{M}$), made during this investigation, showed that the rate constant was approximately the same as that given above. At these lower $OH^{-}$ concentrations, however, the ruthenate formed in the reaction [21] decomposes. The ruthenate decomposition has been studied by Connick and Hurley (29) in the region pH = 10 - 11, and is a disproportionation reaction:

$$3RuO_4^{2-} + (2-x)H_2O \rightleftharpoons 2RuO_4^{-} + RuO_2 \cdot xH_2O + 4OH^{-}. \qquad [23]$$

The equilibrium constant was estimated to be about $10^{-10}$.

The net result of this reaction and reaction [21]--for loss of ruthenate--can be represented as:

$$2RuO_4^{2-} + (2+x)H_2O \longrightarrow 2RuO_2 \cdot xH_2O + 3OH^- + O_2 \ . \qquad [24]$$

In the present perruthenate decomposition studies the rate of decomposition of ruthenate was found to be approximately equal to that of the perruthenate in the range of 0.1-0.2 $\underline{M}$ $OH^-$. At lower alkalinity, ruthenate decomposition was faster than that of perruthenate.

The manganate-permanganate system has been studied by Jezowska-Trzebiatowska and Kalecinski (35,36,37). The decomposition of permanganate (35) at 25°C in 0.88 $\underline{M}$ KOH solution:

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2 \qquad [25]$$

obeys the rate law:

$$\frac{dx}{dt} = k \frac{[MnO_4^-]}{[MnO_4^{2-}]} \qquad [26]$$

where: $k = 2.5 \times 10^{-7}\ \underline{M}\ sec.^{-1}$

The reaction is also first-order with respect to $[OH^-]$. The disproportionation of manganate in 0.0676 $\underline{M}$ KOH at 30°C was also studied by the above authors (36). The reaction

$$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^- \qquad [27]$$

obeys the rate law:

$$\frac{-d[MnO_4^{2-}]}{dt} = k[MnO_4^{2-}]^2 \qquad [28]$$

where: $k = 3.3\ \underline{M}^{-1}\ sec.^{-1}$

The reaction is believed to be proportional to $[OH^-]^{-2}$. The result of reaction [25] followed by reaction [27] gives a net decomposition of manganate represented by

$$3MnO_2^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + O_2 \ . \qquad [29]$$

Reaction [25], the decomposition of permanganate, is inhibited by telluric acid (39). In this investigation, it was found that the decomposition of permanganate is accelerated by ruthenate-perruthenate.

At low concentrations of hydroxide ($< 0.2$ M) the reaction

$$RuO_4^{2-} + 2MnO_4^{2-} + 2H_2O \longrightarrow RuO_2 + 2MnO_4^- + 4OH^- \quad [30]$$

was found, in this investigation, to become significant, which is not surprising because the potential for the reaction becomes positive at about 0.1 M $OH^-$ (39).

Solutions containing ruthenate, perruthenate, manganate, and permanganate decompose within a matter of hours to form nearly colorless solutions which contain finely-divided dark solids, assumed to be hydrated oxides of Ru(IV) and Mn(IV). The rate of decomposition depends upon the cation present, with solutions containing cesium ions decomposing the most rapidly. The order of decomposition rates with the various cations used in this study is

$$Cs^+ > Rb^+ > K^+ \cong Na^+ < Li^+ .$$

Lithium ion is anomalous. The anomaly may be explained by the observations that manganate solutions decompose more rapidly with lithium ion present than with the other four cations and stable manganate solutions could not be prepared in concentrated lithium hydroxide.

## E. Errors

There are several sources of error in this investigation. Spectrophotometry is limited to a maximum accuracy of about 1%, depending upon the magnitude of the absorbancy reading, and introduces an error of about ± 1% in the initial concentrations of the reactants. The error is magnified in determining the extent of reaction since the extent was determined as a difference between two absorbancy readings. For reactions in which the initial concentrations of the two reactants are approximately equal, the difference is nearly as large as the larger of the two absorbancy readings and the error is therefore still about ± 1%. With an increase in the concentration of one reactant over the other the error in determining the extent of reaction increases, because the difference in absorbancy readings becomes small compared to the absorbancy readings themselves.

The greatest source of errors in this investigation is caused by the competing reactions discussed in Section IV-D. At low alkalinity (0.2 M̲ or less), ruthenate begins to oxidize manganate to permanganate. Regardless of whether one follows the loss of manganate at 608 mμ or the formation of ruthenate and permanganate at 507 mμ, the net result of the ruthenate-manganate reaction is an increase in the apparent reaction rate for the perruthenate-manganate system. The error caused by this competition is somewhat greater for solutions in which manganate ion is higher in concentration than ruthenate.

Although the decomposition of permanganate is a competing reaction in all of the rate studies, it does not appear to become significant until the [$OH^-$] reaches about 0.4 M. This decomposition regenerates manganate which has been oxidized by perruthenate. In samples in which the manganate concentration was higher than the perruthenate, the decomposition reaction caused the observed rate constant to be low. Conversely, when the initial perruthenate concentration was higher than that of manganate, manganate regenerated by the permanganate decomposition was reoxidized by perruthenate thus forming still more ruthenate than indicated for the oxidation-reduction reaction under study. Thus the observed rate constant would be high. At high [$OH^-$], the error caused by the permanganate decomposition was ± 10%. In spite of the errors caused by the competing reactions, rate constants determined in duplicate experiments generally agreed to within 2%. The kinetic data were taken during the first 80-85% of each reaction to minimize the complications caused by the competing reactions.

Because of the competing reactions, it was only possible to determine the equilibrium constant for the reaction under investigation between 0.2-0.4 M $OH^-$. The error in the equilibrium constant caused by spectrophotometric error is, at least, 4% when the initial reactant concentrations are equal. When these concentrations differ, the error is magnified. Fortunately, a 10% variation in the equilibrium constant caused a change of only 1% in the calculated rate constants.

The temperature of the reaction was controlled to ± $0.01^{o}C$ and the time was measured from the chart paper which was driven by a synchronous electric motor. Therefore, errors caused by time and temperature were considered negligible.

# V. RESULTS

## A. Determination of the Kinetic Order

The establishment of the rate dependence on the concentration variables is essentially a fitting process as discussed in the Theoretical section of this thesis. It became evident in this investigation that the reaction was reversible. Either the rate constant for the reverse reaction or the equilibrium constant for the reaction had to be established before the kinetic order could be determined. In this system it was easier to determine the equilibrium constant. Because of the competing reactions, it could be determined only over the range of 0.2-0.4 M $OH^-$. The equilibrium constants listed in Table II are for

$$K_{eq} = \frac{[RuO_4^{2-}][MnO_4^-]}{[RuO_4^-][MnO_4^{2-}]} . \qquad [31]$$

It was assumed that the activity coefficients would nearly cancel and therefore $K_{eq}$ should be thermodynamically valid. The value of the potential, $E^0$, for the reaction can be calculated from the relationship:

$$E^0 = \frac{RT}{nF} \ln K \qquad [32]$$

where: R = gas constant

T = absolute temperature

n = number of Faradays

F = Faraday

K = equilibrium constant.

Table II. The equilibrium constant at 20.0°C in various aqueous media

| Medium | Initial concentrations ($\underline{M} \times 10^5$) | | | | |
|---|---|---|---|---|---|
| | $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | $K_{eq}$ |
| 0.405 $\underline{M}$ NaOH | 3.09 | 4.30 | 0.12 | 0.00 | 4.37 |
| 0.405 $\underline{M}$ NaOH | 4.12 | 3.23 | 0.16 | 0.00 | 4.19 |
| 0.405 $\underline{M}$ NaOH | 4.12 | 3.23 | 0.16 | 0.00 | 4.21 |
| 0.405 $\underline{M}$ NaOH | 3.09 | 4.30 | 0.12 | 0.00 | 4.03 |
| 0.199 $\underline{M}$ NaOH + 0.200 $\underline{M}$ $Na_2SO_4$ | 2.52 | 2.35 | 0.05 | 0.02 | 4.67 |
| 0.199 $\underline{M}$ NaOH + 0.200 $\underline{M}$ $Na_2SO_4$ | 2.52 | 2.35 | 0.05 | 0.02 | 4.49 |
| 0.360 $\underline{M}$ KOH | 4.24 | 4.73 | 0.10 | 0.03 | 4.12 |
| 0.360 $\underline{M}$ KOH | 4.45 | 4.41 | 0.10 | 0.02 | 4.31 |
| 0.360 $\underline{M}$ KOH | 4.24 | 4.73 | 0.10 | 0.03 | 3.96 |
| 0.299 $\underline{M}$ NaOH | 3.15 | 3.70 | 0.104 | 0.00 | 4.71 |
| 0.299 $\underline{M}$ NaOH | 3.93 | 2.46 | 0.130 | 0.00 | 4.16 |
| 0.299 $\underline{M}$ NaOH | 3.15 | 3.70 | 0.104 | 0.00 | 4.65 |
| | | | | | 4.32±0.25* |

*Standard deviation of the mean.

The value $\underline{E}^0$ = 0.037 volts has been calculated using the above relationship. By use of the value $\underline{E}^0$ = -0.558 volts (43) for the half-cell:

$$MnO_4^{2-} = MnO_4^- + e^- \qquad [33]$$

the value $\underline{E}^0$ = -0.595 volts at 20°C has been determined for the half cell:

$$RuO_4^{2-} = RuO_4^- + e^- \qquad [34]$$

which is in good agreement with the value of $\underline{E}^0$ = -0.59 volts determined by Connick and Hurley (29).

With a value of 4.32 ± 0.25 for the equilibrium constant at 20.0°C, it was then possible to test the data against various rate laws. As was indicated in the Theoretical section, the data fit the second-order rate law for reversible reactions, first-order in each reactant:

$$\ln \frac{x + (\text{Beta} - Q^{1/2})/\text{gamma}}{x + (\text{Beta} + Q^{1/2})/\text{gamma}} = kQ^{1/2}t + \theta \quad [5]$$

where Beta, gamma, $Q^{1/2}$, and $\theta$ are functions of initial concentrations and are defined in section III-A. Figure 2 shows some typical rate data.

## B. Dependence of the Rate on Nature of the Cation

As was anticipated from the study of manganate-permanganate electron exchange (7), the rate of reaction was found to depend on both the concentration and nature of cation present in the solution. The reaction was carried out in the presence of each of the first five members of

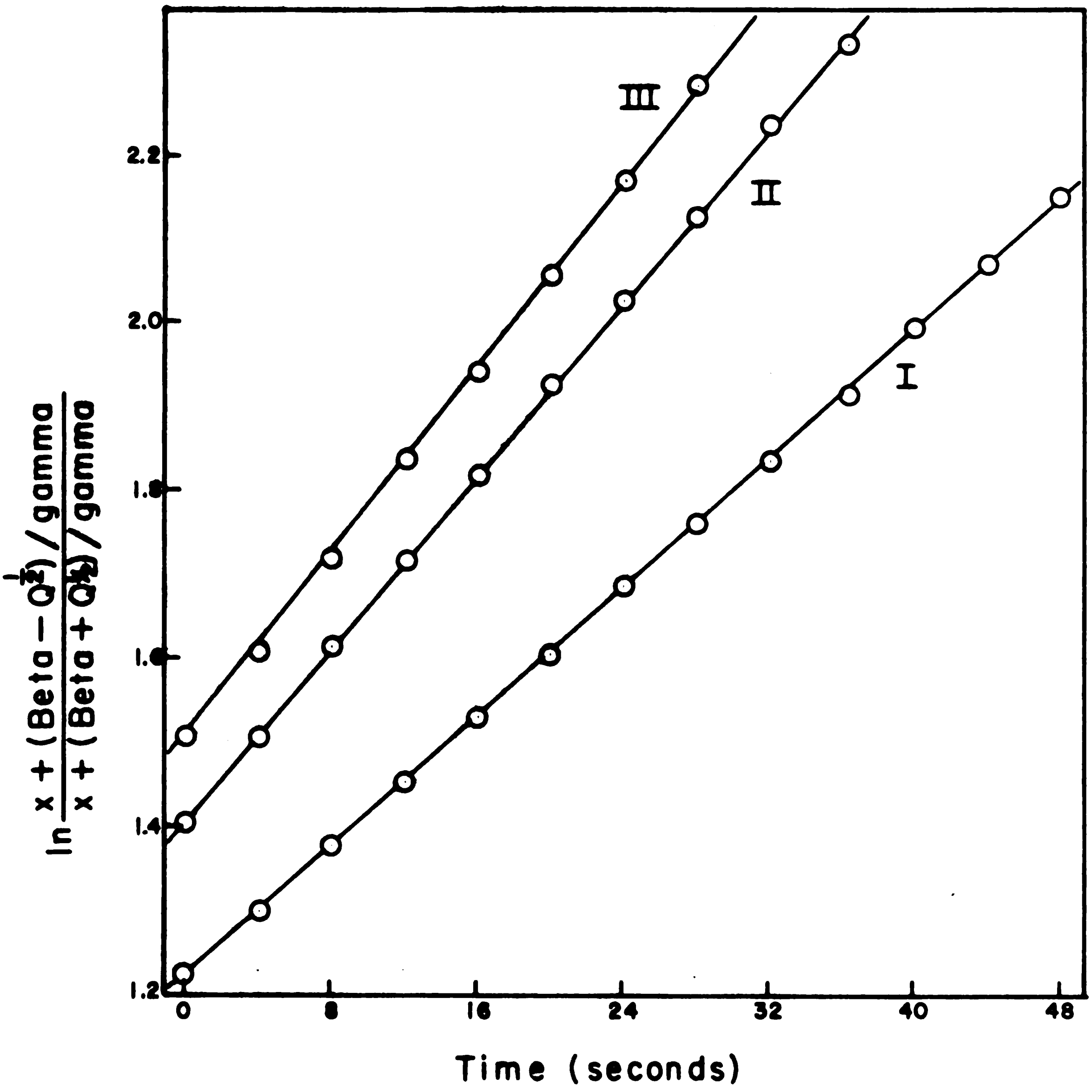

Figure 2. Rate curves for some typical data.

Curve I - 0.189 M LiOH (Table III)
Curve II - 0.299 M NaOH (Table VIII)
Curve III - 0.199 M NaOH + 0.100 M $Rb_2SO_4$ (Table XXIV).

the alkali series and the rate of reaction increased with the size of the cation. The data for the lithium cation are given in Tables III-V, sodium in Tables VI-XVIII, potassium in Tables XIX-XXII, rubidium in Tables XXIII and XXIV, and cesium in Tables XXV and XXVI. The deviation in the rate constants given in the last column of each of the above tables is the percentage variation in the slope of the line (and hence in the rate constant) permitted by one standard deviation of the individual data points. Table XXVII gives a summary of the data from Tables III-XXVI.

Table III. The rate in 0.189 M LiOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 3.49 | 3.87 | 0.00 | 0.04 | 536* | 0.45 |
| 4.66 | 2.90 | 0.00 | 0.03 | 558 | 0.33 |
| 5.82 | 1.94 | 0.00 | 0.02 | 568 | 0.87 |
| 2.33 | 4.84 | 0.00 | 0.05 | 533 | 0.42 |
| 3.49 | 3.87 | 0.00 | 0.04 | 534 | 0.42 |
| 4.66 | 2.90 | 0.00 | 0.03 | 561 | 0.66 |
| | | | | 548±14** | |

*Rate data plotted in Figure 2.

**Standard deviation of the mean.

Table IV. The rate in 0.379 $\underline{M}$ LiOH at 20.0°C

| Initial Concentrations ($\underline{M}$ x $10^5$) | | | | $k_r$ ($\underline{M}^{-1}$sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 3.44 | 4.21 | 0.04 | 0.00 | 648 | 0.67 |
| 2.29 | 5.26 | 0.03 | 0.00 | 637 | 0.79 |
| 3.44 | 4.21 | 0.04 | 0.00 | 680 | 0.92 |
| 4.59 | 3.15 | 0.06 | 0.00 | 713 | 0.39 |
| | | | | 670±29* | |

*Standard deviation of the mean.

Table V. The rate in 0.946 $\underline{M}$ LiOH at 20.0°C

| Initial Concentrations ($\underline{M}$ x $10^5$) | | | | $k_r$ ($\underline{M}^{-1}$sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 4.96 | 3.49 | 0.30 | 0.00 | 1004 | 0.45 |
| 6.62 | 2.62 | 0.40 | 0.00 | 1036 | 1.15 |
| 3.31 | 4.37 | 0.20 | 0.00 | 801 | 0.41 |
| 4.96 | 3.49 | 0.30 | 0.00 | 969 | 1.38 |
| | | | | 953±86* | |

*Standard deviation of the mean.

Table VI. The rate in 0.101 M NaOH at 20.0°C

| Initial Concentrations (M x $10^{-5}$) | | | | $k_r$ ($M^{-1}$sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 3.57 | 6.53 | 0.00 | 0.56 | 472 | 1.55 |
| 5.36 | 5.22 | 0.00 | 0.45 | 508 | 1.23 |
| 7.14 | 3.92 | 0.00 | 0.34 | 527 | 0.75 |
| 8.93 | 2.61 | 0.00 | 0.23 | 523 | 1.11 |
| 8.93 | 2.61 | 0.00 | 0.23 | 501 | 0.63 |
| 3.57 | 6.53 | 0.00 | 0.56 | 426 | 1.34 |
| 2.17 | 7.82 | 0.00 | 0.48 | 466 | 0.67 |
| 3.26 | 6.26 | 0.00 | 0.38 | 457 | 2.10 |
| 5.43 | 3.13 | 0.00 | 0.19 | 442 | 0.85 |
| 4.34 | 4.69 | 0.00 | 0.29 | 451 | 0.60 |
| | | | | 477±33* | |

*Standard deviation of the mean.

Table VII. The rate in 0.202 M NaOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}$ $sec.^{-1}$) | |
| 3.56 | 8.10 | 0.00 | 0.14 | 577 | 0.46 |
| 5.34 | 6.48 | 0.00 | 0.11 | 590 | 0.76 |
| 7.11 | 4.86 | 0.00 | 0.09 | 589 | 0.92 |
| 8.89 | 3.24 | 0.00 | 0.06 | 623 | 0.33 |
| 7.11 | 4.86 | 0.00 | 0.09 | 598 | 0.43 |
| 5.34 | 6.48 | 0.00 | 0.11 | 605 | 1.25 |
| 1.87 | 2.06 | 0.21 | 0.00 | 530 | 0.75 |
| 1.24 | 2.58 | 0.14 | 0.00 | 515 | 2.68 |
| 2.49 | 1.55 | 0.29 | 0.00 | 565 | 1.59 |
| 3.11 | 1.03 | 0.36 | 0.00 | 605 | 1.24 |
| 2.49 | 1.55 | 0.29 | 0.00 | 552 | 1.02 |
| 1.87 | 2.06 | 0.21 | 0.00 | 537 | 1.20 |
| | | | | 573±33* | |

*Standard deviation of the mean.

Table VIII. The rate in 0.299 M NaOH at 20.0°C

| Initial Concentrations ($M \times 10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 4.23 | 2.71 | 0.00 | 0.01 | 714* | 0.46 |
| 5.64 | 2.03 | 0.00 | 0.01 | 735 | 1.32 |
| 2.82 | 3.39 | 0.00 | 0.01 | 683 | 0.37 |
| 3.15 | 3.70 | 0.10 | 0.00 | 737 | 0.43 |
| 3.15 | 3.70 | 0.10 | 0.00 | 742 | 0.51 |
| | | | | 722±26** | |

*Rate data plotted in Figure 2.

**Standard deviation of the mean.

Table IX. The rate in 0.405 M NaOH at 20°C

| Initial Concentrations ($M \times 10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.06 | 5.38 | 0.08 | 0.00 | 761 | 1.41 |
| 3.09 | 4.30 | 0.12 | 0.00 | 772 | 0.64 |
| 4.12 | 3.23 | 0.16 | 0.00 | 778 | 0.72 |
| 5.15 | 2.15 | 0.20 | 0.00 | 780 | 0.56 |
| 4.12 | 3.23 | 0.16 | 0.00 | 759 | 0.64 |
| 3.09 | 4.30 | 0.12 | 0.00 | 758 | 0.48 |
| | | | | 766±9* | |

*Standard deviation of the mean.

Table X. The rate in 0.608 $\underline{M}$ NaOH at 20°C

| Initial Concentrations ($\underline{M}$ x $10^5$) | | | | $k_r$ | Percent standard |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($\underline{M}^{-1}sec.^{-1}$) | deviation |
| 2.09 | 4.85 | 0.12 | 0.06 | 874 | 1.55 |
| 3.13 | 3.88 | 0.18 | 0.06 | 903 | 0.62 |
| 4.17 | 2.91 | 0.24 | 0.04 | 932 | 1.01 |
| 5.22 | 1.94 | 0.29 | 0.03 | 972 | 0.32 |
| 4.17 | 2.91 | 0.24 | 0.04 | 963 | 0.81 |
| 3.13 | 3.88 | 0.18 | 0.05 | 950 | 0.29 |
| | | | | 932±34* | |

*Standard deviation of the mean.

Table XI. The rate in 0.697 $\underline{M}$ NaOH at 20.0°C

| Initial Concentrations ($\underline{M}$ x $10^5$) | | | | $k_r$ | Percent standard |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($\underline{M}^{-1}sec.^{-1}$) | deviation |
| 1.14 | 3.60 | 0.96 | 0.00 | 900 | 1.20 |
| 1.52 | 2.70 | 1.28 | 0.00 | 1051 | 1.51 |
| 1.89 | 1.80 | 1.60 | 0.00 | 1060 | 0.39 |
| 2.27 | 0.90 | 1.92 | 0.00 | 1231 | 2.61 |
| | | | | 1061±110* | |

*Standard deviation of the mean.

Table XII. The rate in 1.01 M NaOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ ($M^{-1}$ sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 1.87 | 4.38 | 1.01 | 0.03 | 1085 | 0.94 |
| 2.50 | 3.29 | 1.34 | 0.02 | 1077 | 1.05 |
| 3.12 | 2.19 | 1.68 | 0.01 | 1164 | 1.69 |
| 2.50 | 3.29 | 1.34 | 0.02 | 1084 | 2.51 |
| 1.87 | 4.38 | 1.01 | 0.03 | 1044 | 2.31 |
| | | | | 1091±40* | |

*Standard deviation of the mean.

Table XIII. The rate in 0.199 M NaOH + 0.100 M $Na_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ ($M^{-1}$ sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 1.91 | 3.50 | 0.06 | 0.03 | 681 | 0.69 |
| 1.91 | 3.50 | 0.06 | 0.03 | 670 | 0.95 |
| 2.54 | 2.62 | 0.08 | 0.03 | 684 | 1.09 |
| 2.54 | 2.62 | 0.08 | 0.03 | 688 | 0.97 |
| 3.18 | 1.75 | 0.10 | 0.02 | 698 | 1.08 |
| 1.27 | 4.37 | 0.04 | 0.04 | 668 | 0.92 |
| | | | | 682±20* | |

*Standard deviation of the mean.

Table XIV. The rate in 0.199 M NaOH + 0.200 M $Na_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 1.89 | 3.13 | 0.04 | 0.03 | 912 | 0.74 |
| 2.52 | 2.35 | 0.05 | 0.02 | 870 | 1.32 |
| 3.15 | 1.56 | 0.06 | 0.01 | 961 | 0.55 |
| 1.26 | 3.91 | 0.02 | 0.03 | 908 | 0.77 |
| 1.89 | 3.13 | 0.04 | 0.03 | 908 | 1.07 |
| 2.52 | 2.35 | 0.05 | 0.02 | 948 | 0.89 |
| | | | | 917±30* | |

*Standard deviation of the mean.

Table XV. The rate in 0.199 M NaOH + 0.300 M $Na_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 1.90 | 3.33 | 0.05 | 0.03 | 977 | 0.45 |
| 2.53 | 2.50 | 0.06 | 0.02 | 1058 | 1.68 |
| 1.90 | 3.33 | 0.05 | 0.03 | 1000 | 2.05 |
| 2.53 | 2.50 | 0.06 | 0.02 | 1063 | 0.82 |
| 3.16 | 1.67 | 0.08 | 0.01 | 1074 | 1.53 |
| 1.27 | 4.17 | 0.03 | 0.04 | 1001 | 2.71 |
| | | | | 1029±37* | |

*Standard deviation of the mean.

Table XVI. The rate in 0.199 M NaOH + 0.200 M $Na_3PO_4$ at 20.0°C

| Initial Concentrations ($M \times 10^5$) | | | | $k_r$ ($M^{-1}$ sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 1.92 | 3.12 | 0.04 | 0.00 | 865 | 1.41 |
| 2.56 | 2.34 | 0.05 | 0.00 | 926 | 0.59 |
| 3.19 | 1.56 | 0.07 | 0.00 | 920 | 1.24 |
| 1.28 | 3.90 | 0.03 | 0.00 | 860 | 1.54 |
| 1.92 | 3.12 | 0.04 | 0.00 | 918 | 1.20 |
| 2.56 | 2.34 | 0.05 | 0.00 | 938 | 0.62 |
| | | | | 904±30* | |

*Standard deviation of the mean.

Table XVII. The rate in 0.199 M NaOH + 0.600 M $NaNO_3$ at 20.0°C

| Initial Concentrations ($M \times 10^5$) | | | | $k_r$ ($M^{-1}$ sec.$^{-1}$) | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | | |
| 3.59 | 2.75 | 0.02 | 0.01 | 1014 | 1.41 |
| 2.69 | 3.67 | 0.02 | 0.02 | 979 | 0.93 |
| 3.59 | 2.75 | 0.02 | 0.01 | 1001 | 0.94 |
| | | | | 998±20* | |

*Standard deviation of the mean.

Table XVIII. The rate in 0.199 M NaOH + 0.600 M $NaClO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 3.61 | 3.10 | 0.03 | 0.00 | 1047 | 1.21 |
| 2.71 | 4.14 | 0.03 | 0.00 | 1002 | 0.59 |
| 3.61 | 3.10 | 0.03 | 0.00 | 1038 | 0.75 |
| | | | | 1029±20* | |

*Standard deviation of the mean.

Table XIX. The rate in 0.090 M KOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 6.18 | 2.85 | 0.00 | 0.21 | 612 | 0.85 |
| 4.95 | 4.28 | 0.00 | 0.32 | 616 | 0.97 |
| 3.71 | 5.71 | 0.00 | 0.42 | 612 | 0.92 |
| 2.47 | 7.14 | 0.00 | 0.53 | 609 | 0.09 |
| 4.95 | 4.28 | 0.00 | 0.32 | 620 | 1.43 |
| 6.18 | 2.85 | 0.00 | 0.21 | 622 | 1.96 |
| | | | | 615±4* | |

*Standard deviation of the mean.

Table XX. The rate in 0.180 M KOH at 20.0$^{0}$C.

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.48 | 7.27 | 0.01 | 0.10 | 807 | 3.02 |
| 3.71 | 5.81 | 0.01 | 0.08 | 809 | 1.04 |
| 2.48 | 7.27 | 0.01 | 0.10 | 786 | 0.34 |
| 4.95 | 4.36 | 0.01 | 0.06 | 794 | 0.89 |
| 6.19 | 2.91 | 0.01 | 0.04 | 794 | 1.07 |
| 4.95 | 4.36 | 0.01 | 0.06 | 765 | 1.45 |
| 4.95 | 4.36 | 0.01 | 0.06 | 794 | 0.91 |
| | | | | 793±14* | |

*Standard deviation of the mean.

Table XXI. The rate in 0.360 M KOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 3.18 | 6.30 | 0.07 | 0.03 | 1018 | 1.01 |
| 4.24 | 4.73 | 0.10 | 0.03 | 1011 | 0.98 |
| 5.30 | 3.15 | 0.12 | 0.02 | 1081 | 0.39 |
| 4.45 | 4.41 | 0.10 | 0.02 | 1036 | 0.80 |
| 4.24 | 4.73 | 0.10 | 0.03 | 1031 | 0.82 |
| | | | | 1035±22* | |

*Standard deviation of the mean.

Table XXII. The rate in 0.720 M KOH at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.87 | 4.58 | 0.35 | 0.00 | 1413 | 1.21 |
| 3.82 | 3.43 | 0.47 | 0.00 | 1618 | 0.40 |
| 2.87 | 4.58 | 0.35 | 0.00 | 1453 | 0.65 |
| 3.57 | 3.74 | 0.44 | 0.00 | 1579 | 1.15 |
| 1.91 | 5.72 | 0.23 | 0.00 | 1480 | 0.48 |
| 3.82 | 3.43 | 0.47 | 0.00 | 1586 | 1.68 |
| | | | | 1521±76* | |

*Standard deviation of the mean.

Table XXIII. The rate in 0.199 M NaOH + 0.05 M $Rb_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.765 | 2.295 | 0.355 | 0.022 | 835 | 0.95 |
| 2.21 | 3.44 | 0.284 | 0.033 | 831 | 0.87 |
| 2.765 | 2.295 | 0.355 | 0.022 | 837 | 0.86 |
| | | | | 834 ± 3* | |

*Standard deviation of the mean.

Table XXIV. The rate in 0.199 M NaOH + 0.10 M $Rb_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.835 | 1.805 | 0.284 | 0.015 | 1093* | 0.79 |
| 2.27 | 2.71 | 0.227 | 0.022 | 983 | 0.78 |
| 2.27 | 2.71 | 0.227 | 0.022 | 989 | 0.75 |
| | | | | 1022±51** | |

*Rate data plotted in Figure 2.

**Standard deviation of the mean.

Table XXV. The rate in 0.199 M NaOH + 0.050 M $Cs_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.78 | 2.22 | 0.317 | 0.02 | 1075 | 1.80 |
| 2.22 | 3.33 | 0.254 | 0.03 | 1118 | 0.64 |
| | | | | 1097±22* | |

*Standard deviation of the mean.

Table XXVI. The rate in 0.199 M NaOH + 0.100 M $Cs_2SO_4$ at 20.0°C

| Initial Concentrations (M x $10^5$) | | | | $k_r$ | Percent standard deviation |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | ($M^{-1}sec.^{-1}$) | |
| 2.78 | 2.405 | 0.308 | 0.01 | 1451 | 0.83 |
| 2.22 | 3.61 | 0.246 | 0.015 | 1462 | 0.77 |
| 2.78 | 2.405 | 0.308 | 0.01 | 1469 | 0.71 |
| | | | | 1461±8* | |

*Standard deviation of the mean.

Table XXVII. Summary of the rate at 20.0°C

| Concentrations (moles/liter) | | | $k_r$ |
|---|---|---|---|
| Cation | Hydroxide | Anion | ($\underline{M}^{-1}$ sec.$^{-1}$) |
| 0.189 $Li^+$ | 0.189 | -- | 548±14 |
| 0.379 $Li^+$ | 0.379 | -- | 670±29 |
| 0.946 $Li^+$ | 0.946 | -- | 953±86 |
| 0.101 $Na^+$ | 0.101 | -- | 477±33 |
| 0.202 $Na^+$ | 0.202 | -- | 573±33 |
| 0.299 $Na^+$ | 0.299 | -- | 722±26 |
| 0.405 $Na^+$ | 0.405 | -- | 766± 9 |
| 0.608 $Na^+$ | 0.608 | -- | 932±34 |
| 0.697 $Na^+$ | 0.697 | -- | 1061±110 |
| 1.01 $Na^+$ | 1.01 | -- | 1091±40 |
| 0.399 $Na^+$ | 0.199 | 0.100 $SO_4^{2-}$ | 682±10 |
| 0.599 $Na^+$ | 0.199 | 0.200 $SO_4^{2-}$ | 917±30 |
| 0.799 $Na^+$ | 0.199 | 0.300 $SO_4^{2-}$ | 1029±37 |
| 0.799 $Na^+$ | 0.199 | 0.200 $PO_4^{3-}$ | 904±30 |
| 0.799 $Na^+$ | 0.199 | 0.600 $NO_3^-$ | 998±20 |
| 0.799 $Na^+$ | 0.199 | 0.600 $ClO_4^-$ | 1029±20 |
| 0.090 $K^+$ | 0.090 | -- | 615± 4 |
| 0.180 $K^+$ | 0.180 | -- | 794±14 |
| 0.360 $K^+$ | 0.360 | -- | 1035±22 |
| 0.720 $K^+$ | 0.720 | -- | 1521±22 |
| 0.199 $Na^+$<br>0.100 $Rb^+$ | 0.199 | 0.050 $SO_4^{2-}$ | 834± 3 |
| 0.199 $Na^+$<br>0.200 $Rb^+$ | 0.199 | 0.100 $SO_4^{2-}$ | 1022±51 |
| 0.199 $Na^+$<br>0.100 $Cs^+$ | 0.199 | 0.050 $SO_4^{2-}$ | 1097±22 |
| 0.199 $Na^+$<br>0.200 $Cs^+$ | 0.199 | 0.100 $SO_4^{2-}$ | 1461± 8 |

## C. Dependence of the Rate on Ionic Strength

The rate of reaction was more sensitive to the concentration of the cation than to ionic strength. Marcus' treatment (Section III-B) indicates that a plot of ln $k_r$ *vs* $e^{-\kappa r}$ should be linear and that the rate should increase with increasing ionic strength for a positive charge product, $e_1e_2$. Examination of the data in Table XXVIII shows there is, if anything, a slight decrease in rate with an increase in ionic strength when the concentration of cation is held constant. The accuracy of the rate data does not show whether or not the decrease is significant.

Table XXVII. Dependence of the rate on ionic strength in sodium hydroxide solutions at 20.0°C

| Concentrations (moles/liter) | | | | $k_r$ |
|---|---|---|---|---|
| Hydroxide | Anion | $Na^+$ | $\mu$ | ($M^{-1}$sec.$^{-1}$) |
| 0.405 | -- | 0.405 | 0.405 | 766± 9 |
| 0.199 | 0.100 $SO_4^{2-}$ | 0.399 | 0.499 | 682±10 |
| 0.608 | -- | 0.608 | 0.608 | 932±34 |
| 0.199 | 0.200 $SO_4^{2-}$ | 0.599 | 0.799 | 917±30 |
| 0.199 | 0.600 $NO_3^-$ | 0.799 | 0.799 | 998±20 |
| 0.199 | 0.600 $ClO_4^-$ | 0.799 | 0.799 | 1029±20 |
| 0.199 | 0.300 $SO_4^{2-}$ | 0.799 | 1.099 | 1029±37 |
| 0.199 | 0.200 $PO_4^{3-}$ | 0.799 | 1.399 | 904±30 |

## D. Dependence of the Equilibrium Constant on Temperature

The equilibrium constant depends markedly on temperature. The equilibrium data are given in Table XXIX. It is possible to determine the enthalpy of reaction, $\Delta H^0$, from the relationship:

$$\ln K_{eq} = \frac{-\Delta H^0}{RT} + \text{constant} \qquad [33]$$

if one assumes that $\Delta H^0$ is constant over the temperature range. The data are plotted in Figure 3, $\Delta H^0 = 3950$ cal/mole, and $\Delta S^0$ can be calculated from

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad [34]$$

where: $\Delta G^0 = - RT\ln K_{eq}$

$\Delta G^0 = - 850$ cal/mole

and $\Delta S^0 = -10.6$ e.u. at 20.0°C.

## E. Dependence of the rate on Temperature

The temperature dependence of the rate was studied in only one medium, 0.30 M NaOH. The data obtained are given in Table XXX. The activation energy, $E_a$, can be obtained from the relationship:

$$\ln k_r = - \frac{E_a}{RT} + \text{constant} \qquad [35]$$

and $E_a = 7.65$ kcal/mole (Figure 4). The data can be interpreted by the transition state equation (18):

$$k_r = (kT/h)\exp[\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT] \qquad [36]$$

where: $k_r$ = rate constant

$k$ = Boltzmann's constant

Table XXIX. Dependence of the equilibrium constant on temperature

| Initial concentrations ($\underline{M}$ x $10^5$) | | | | | |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | T($^0$C) | $K_{eq}$ |
| 3.13 | 3.685 | 0.130 | 0.018 | 14.3 | 5.26 |
| 3.13 | 3.685 | 0.130 | 0.018 | 14.3 | 5.18 |
| | From Table II | | | 20.0 | 4.32±0.25 |
| 3.15 | 3.70 | 0.104 | 0.00 | 24.7 | 3.90 |
| 3.93 | 2.46 | 0.130 | 0.00 | 24.7 | 4.22 |
| 3.15 | 3.70 | 0.104 | 0.00 | 24.7 | 4.11 |
| 3.14 | 3.67 | 0.124 | 0.018 | 32.0 | 3.54 |
| 3.92 | 2.45 | 0.155 | 0.012 | 32.0 | 3.36 |
| 3.14 | 3.67 | 0.124 | 0.018 | 32.0 | 3.57 |

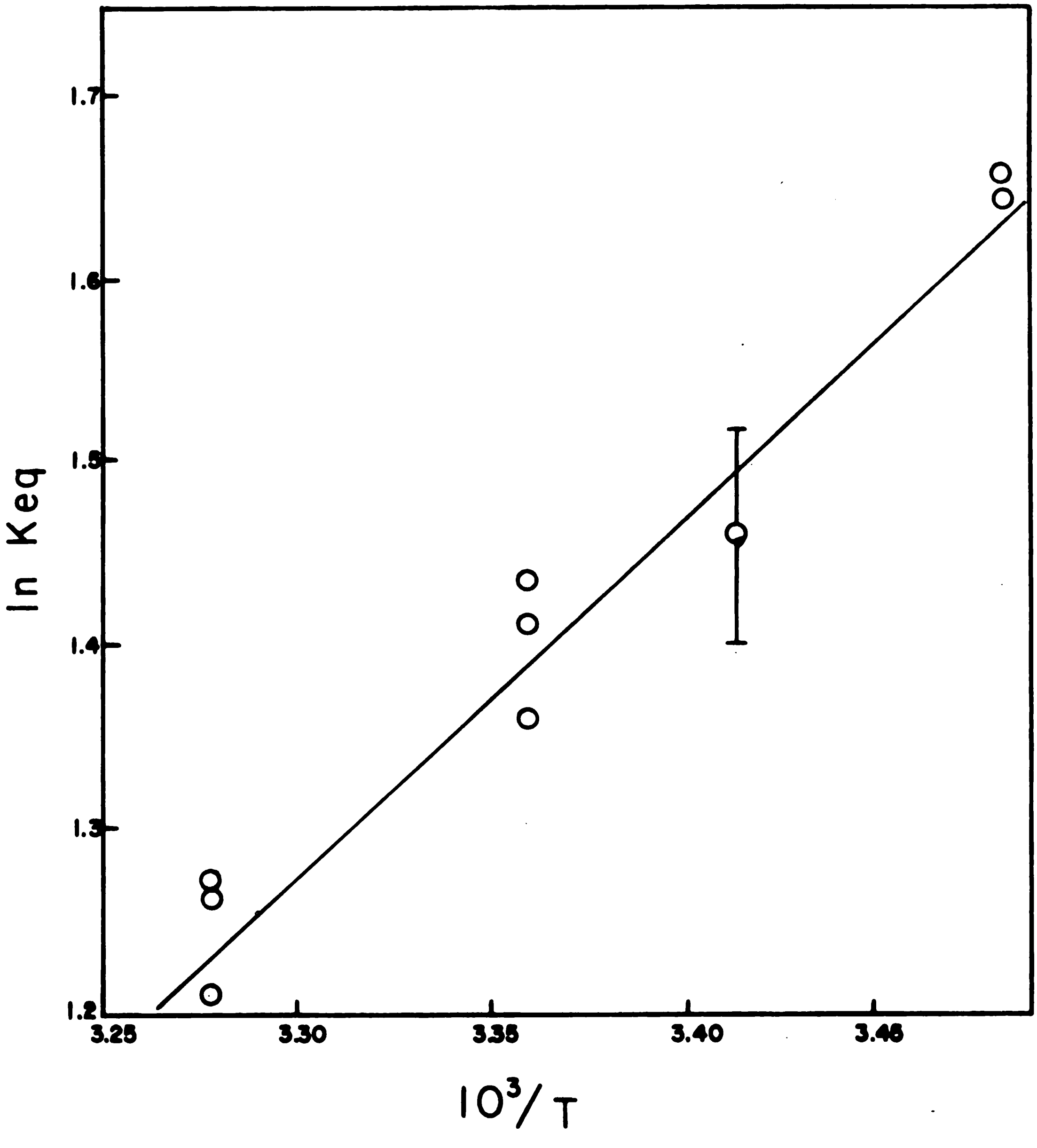

Figure 3. Temperature dependence of the equilibrium constant in 0.299 M NaOH.

Table XXX. Dependence of the rate on temperature in 0.299 M NaOH

| Initial Concentrations ($M \times 10^5$) | | | | | $k_r$ |
|---|---|---|---|---|---|
| $RuO_4^-$ | $MnO_4^{2-}$ | $RuO_4^{2-}$ | $MnO_4^-$ | T(°C) | ($M^{-1}$ sec.$^{-1}$) |
| 3.13 | 3.685 | 0.130 | 0.018 | 14.3 | 572 |
| 3.92 | 2.455 | 0.163 | 0.012 | 14.3 | 587 |
| 3.13 | 3.685 | 0.130 | 0.018 | 14.3 | 573 |
| 3.92 | 2.455 | 0.163 | 0.012 | 14.3 | 576 |
| | See Table VIII | | | 20.0 | 722±26 |
| 3.15 | 3.70 | 0.104 | 0.00 | 24.7 | 902 |
| 3.93 | 2.46 | 0.130 | 0.00 | 24.7 | 905 |
| 3.15 | 3.70 | 0.104 | 0.00 | 24.7 | 904 |
| 3.92 | 2.45 | 0.155 | 0.012 | 32.0 | 1227 |
| 3.14 | 3.67 | 0.124 | 0.018 | 32.0 | 1301 |

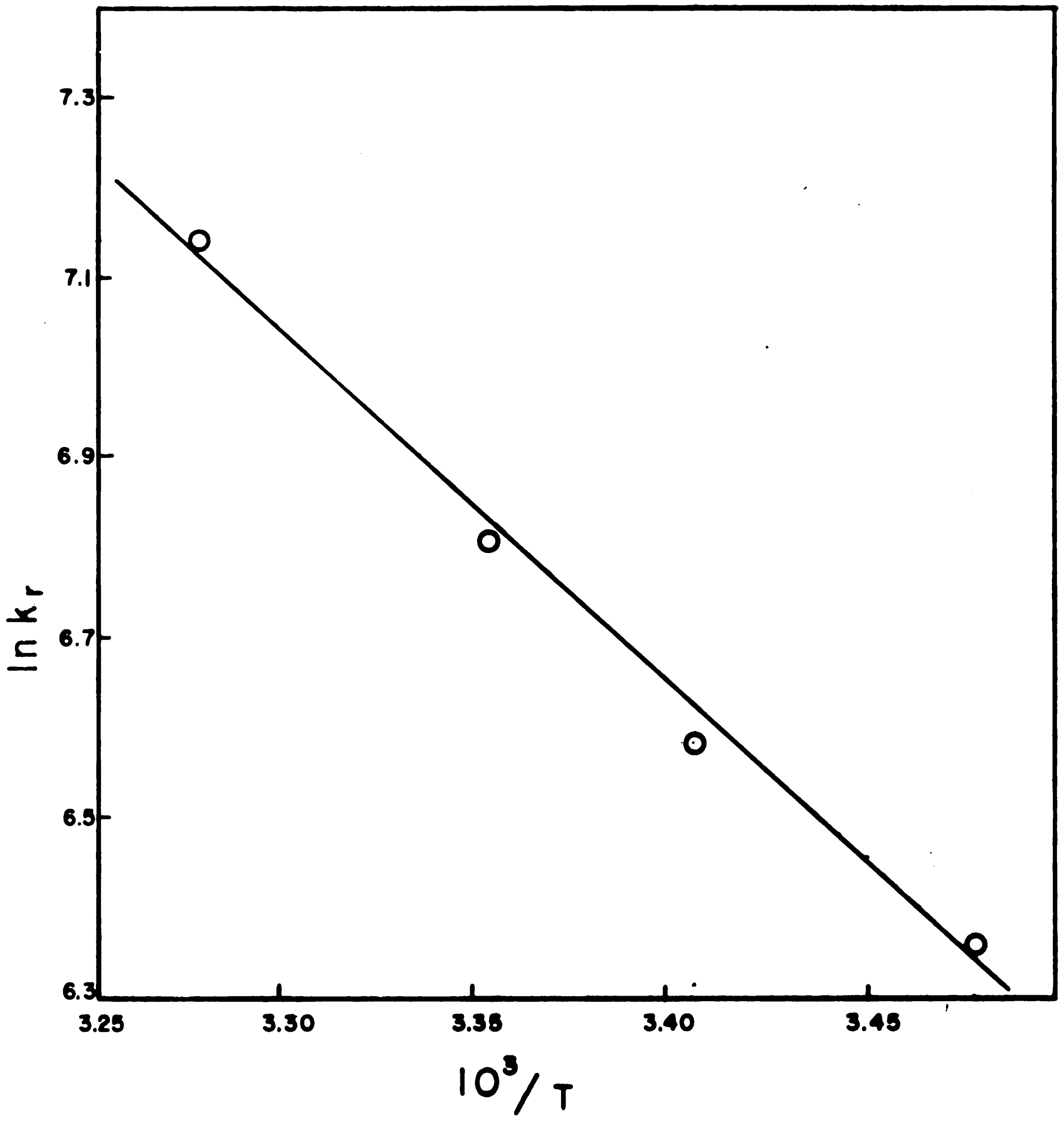

Figure 4. Temperature dependence of the rate constant in 0.299 M NaOH.

$h$ = Planck's constant

$T$ = absolute temperature

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

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

$R$ = gas constant

$E_a$ = activation energy per mole

$\Delta H^{\ddagger} = E_a - RT$ (for reactions in solution)

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ .

From the above relationships, $\Delta H^{\ddagger} = 7.07$ kcal/mole, $\Delta S^{\ddagger} = -10.7$ e.u., and $\Delta G^{\ddagger} = 10.2$ kcal/mole.

# VI. DISCUSSION

The values obtained for $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$ were not anticipated. The entropy change for the reaction

$$RuO_4^- + MnO_4^{2-} \rightleftharpoons RuO_4^{2-} + MnO_4^- \qquad [37]$$

would be expected to be near zero. The value $\Delta S^0 = 1.7$ e.u. for the above reaction is calculated from the empirical formula (40):

$$S^0(MO_n^{-Z}) = 40.2 + \frac{3}{2} R \ln A - \frac{27.2\ Z^2}{0.25\ nr_0} \qquad [38]$$

where:

$n$ = number of "bare oxygen atoms

$Z$ = charge on the anion

$A$ = molecular weight of the anion

$r_0$ = M-O distance + 1.40 Å.

The experimental result of $\Delta S^0 = -10.6$ e.u. is much too different from the calculated value of $\Delta S^0 = 1.7$ e.u. to attribute to experimental error. It was suggested to the author that one or more of the anions could possibly have associated hydroxide ion (41). Hydroxide ion association can be represented by the following equilibrium:

$$MO_4^{x-} + OH^- \rightleftharpoons MO_4OH^{(x+1)-} \qquad [39]$$

where $M$ is Ru or Mn and $x$ is 1 or 2, depending on the oxidation state. The negative value of $\Delta S^0$ for reaction [37] suggests that the equilibrium constants for reaction [39] are larger for ruthenate and permanganate than perruthenate and manganate because reaction [39] would have a large negative entropy. The equilibrium constant for reaction [39] should also be larger for permanganate than ruthenate because of size and charge contribution to electrostatic repulsion.

Comparison of the experimental rate constant with the rate constants calculated from Marcus' equations is of interest. A summary of the necessary calculations may be found in the Theoretical section of this thesis. From Marcus' equations (for reaction in solution of 0.20 ionic strength):

$k_r = 7.8 \times 10^4\ \underline{M}^{-1}\text{sec.}^{-1}$ ($r$ = 5.76 Å, crystal radii)

$k_r = 6.2 \times 10^7\ \underline{M}^{-1}\text{sec.}^{-1}$ ($r$ = 10.14 Å, water molecule interposed).

The experimentally determined rate constant for reaction in 0.20 $\underline{M}$ sodium hydroxide solution was (Table XXVII):

$k_r = 5.7 \times 10^2\ \underline{M}^{-1}\text{sec.}^{-1}$

The agreement between the experimental value and the calculated value for $\underline{r}$ = 5.76 Å is as good as can be expected. The estimate of the rearrangement energy is undoubtedly low, especially in view of the possible hydroxide ion association with one or more of the anions. The increase in rate by a factor of 1.10 predicted from Marcus' equations for a change in ionic strength from 0.405 to 0.499 was not observed (Table XXVIII). In fact, there may be a slight decrease in rate with increasing ionic strength at constant sodium and hydroxide concentrations. The increase in the rate with size and concentration of the alkali-metal cation can probably be attributed to the ion-pairing abilities of the larger cations; the larger cations shield the anions from each other. The observed rate of reaction is thus affected by both ion-pairing and association of the anions with hydroxide. One cannot assess the contribution to the rate made by these factors at present.

A comparison of the results from this investigation with those obtained from the manganate-permanganate (7) and ruthenate-perruthenate (Appendix) system is worthwhile. In the manganate-permanganate exchange reaction Sheppard and Wahl found for 0°C and 0.16 M sodium hydroxide:

$$k_r = 710\ \underline{M}^{-1}\text{sec.}^{-1}\ .$$

In the ruthenate-perruthenate exchange reaction, a value of

$$k_r > 10^4\ \underline{M}^{-1}\text{sec.}^{-1}$$

for 0°C and 0.10 M sodium hydroxide has been estimated. For the "mixed" system of manganate-perruthenate a value of

$$k_r = 220\ \underline{M}^{-1}\text{sec.}^{-1}$$

is calculated for 0°C and 0.20 M sodium hydroxide from the rate at 20.0°C and $\underline{E_a}$ = 7.65 kcal/mole. We note that the manganate-perruthenate reaction is slower than either of the two exchange reactions. The $\underline{m}$ factor in the Marcus theory would suggest a higher rate for the manganate-perruthenate reaction since the value of $\underline{\Delta G^0}$ is negative, whereas the value of $\underline{\Delta G}^0$ for the exchange systems is about zero. On the other hand, the manganate-perruthenate reaction may have a higher energy of rearrangement which would predict a lower rate of reaction. In addition, the electronic vibrational levels of the ruthenium and manganese species do not coincide so that the transmission probability for the electron within the activated complex for manganate-perruthenate is probably lower than the transmission probability in either ruthenate-perruthenate or manganate-permanganate. The lower rate in the manganate-permanganate system in comparison to the ruthenate-perruthenate system might be attributed to the association of permanganate with hydroxide. Hydroxide association is consistent with the negative value found for $\underline{\Delta S}^0$ in the manganate-perruthenate system.

The values of the activation energy and the entropy and free energy of activation for the manganate-permanganate reaction were determined by Sheppard and Wahl (7) to be

$$E_a = 10.5 \text{ kcal.}$$

$$\Delta S^{\ddagger} = -9 \text{ e.u.}$$

$$\Delta F^{\ddagger} = 12.4 \text{ kcal/mole}$$

for 0°C and 0.16 $\underline{M}$ sodium hydroxide solution. For the manganate-perruthenate system

$$E_a = 7.6 \text{ kcal.}$$

$$\Delta S^{\ddagger} = -10.7 \text{ e.u.}$$

$$\Delta F^{\ddagger} = 10.2 \text{ kcal/mole}$$

for 20.0°C and 0.30 M sodium hydroxide solution. The differences can be attributed, at least in part, to experimental error and to the different concentrations of sodium hydroxide. One would expect, however, that the entropy of activation would be more negative for the manganate-perruthenate system, as is observed.

A comparison of the cation effect in the manganate-permanganate and manganate-perruthenate reactions shows that the former is more sensitive to the size and concentration of the cation. For example, increasing the sodium ion concentration from 0.16 M to 0.99 M increases the rate of the manganate-permanganate reaction by a factor of 2.4. In the manganate-perruthenate reaction, a similar increase in sodium ion concentration (0.20 M to 1.0 M) increases the rate of reaction by a factor of 2.1. Similarly, the reaction rate in manganate-permanganate is nearly doubled by changing from 0.57 M sodium to 0.57 M potassium ion. The rates of reaction for similar concentrations, interpolated from the rate data (Table XXVII), indicate that potassium ion is only 40% more effective than sodium ion in the manganate-perruthenate reaction.

In the manganate-perruthenate reaction the entropy of reaction, $\Delta S^0$ = -10.6 e.u., is essentially the same as the entropy of activation, $\Delta S^{\ddagger}$ = -10.7 e.u. Considering experimental error, it is possible to estimate the difference between the two entropies as high as 2 e.u. Thus the major part of the entropy of activation is the entropy of reaction which is, perhaps, not unreasonable when one considers that the reaction is slower than predicted by Marcus' equations. The major factor in the lower rate of reaction could then be the entropy of reaction.

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# APPENDIX

# THE ELECTRON EXCHANGE BETWEEN PERRUTHENATE AND RUTHENATE IN ALKALINE AQUEOUS SOLUTION

A preliminary study of the electron exchange between ruthenate and perruthenate showed that the exchange was too fast to measure by the available techniques.

Stock solutions were prepared as described in Section IV-A of this thesis. The $^{106}$Ru tracer was obtained as Ru-106-Rh-106, carrier free, from Oak Ridge National Laboratory as $RuCl_3$ in 6 $\underline{M}$ HCl. It was added to one sample of Ru(III) in 3 $\underline{M}$ $H_2SO_4$ before the sodium bismuthate oxidation. The concentrations of ruthenate and perruthenate in stock solutions were determined spectrophotometrically as described above (Section IV-B).

The experiments, in which perruthenate was separated from the exchanging mixture, perruthenate solutions were added to ruthenate, both in 0.10 $\underline{M}$ NaOH, at $0^0$C and the mixture was mechanically stirred. A quench solution consisting of 4.00 ml of 0.1 $\underline{M}$ tetraphenylarsonium chloride in 0.1 $\underline{M}$ perrhenate ($ReO_4^-$, a non-isotopic carrier) was added. The precipitate was removed by suction and the supernatant liquid was reserved for counting. When it had been learned that exhange was very rapid, several experiments were carried out with the quench solution added before the perruthenate and the solution was stirred vigorously during the addition.

In an effort to determine that the fast exchange was not due to separation induced exchange, a second series of experiments was carried out in which ruthenate was precipitated. In these experiments ruthenate was added to stirred perruthenate at $0^oC$ in 0.1 $\underline{M}$ NaOH. A quench solution was prepared with 4.00 ml of saturated $Ba(OH)_2$ plus 5.00 ml of 0.01 $\underline{M}$ $Na_2SO_4$ and was added rapidly to the exchange mixture. The $BaRuO_4$-$BaSO_4$ was filtered off and the filtrate was reserved for counting.

Two-milliliter samples of the various supernatant liquids were placed in one dram, screw-cap vials and were counted in an integral, well-type, scintillation counter. The energetic gamma rays (0.51-2.4 M.e.V.) from the $^{106}Rh$ daughter were counted after the solutions reached radioactive equilibrium (a few minutes are required).

In all experiments conducted, even those with the quench added before the reagents were mixed, complete exchange was observed in the time of mixing and separating, which is estimated to be 5-15 seconds for precipitation and another 10-40 seconds for the filtration. Thus the exchange must be complete in less than 5 seconds, if there is no exchange between precipitates and the supernatant liquids.

In experiments in which perruthenate was precipitated, the solutinns were $2.5 \times 10^{-5}$ $\underline{M}$ in $RuO_4^{2-}$, $4.9 \times 10^{-5}$ $\underline{M}$ in $RuO_4^-$, and 0.10 $\underline{M}$ in NaOH. Thus a second order rate constant of $1.7 \times 10^3$ $\underline{M}^{-1}sec.^{-1}$ is a lower limit. By similar experimental procedures, Sheppard and Wahl (7) measured half-times as short as 0.25 seconds in the manganate-permanganate exchange reaction. Thus is seems the exchange would be even faster and a rate constant of $3.3 \times 10^4$ $\underline{M}^{-1}sec.^{-1}$ is suggested.

In experiments in which ruthenate was precipitated, concentrations were $2.8 \times 10^{-5}$ $\underline{M}$ in $RuO_4^{2-}$, $2.95 \times 10^{-5}$ $\underline{M}$ in $RuO_4^-$, and 0.10 $\underline{M}$ in NaOH. These figures suggest a second order rate constant of $2.5 \times 10^3$ $\underline{M}^{-1}sec.^{-1}$ for a 5 second half-time and $4.8 \times 10^4$ $\underline{M}^{-1}sec.^{-1}$ for 0.25 second.

Electron spin resonance measurements were made on solutions of $2.0 \times 10^{-2}$ $\underline{M}$ $RuO_4^{2-}$ in 2.0 $\underline{M}$ NaOH and $1.0 \times 10^{-2}$ $\underline{M}$ $RuO_4^-$ in 1.0 $\underline{M}$ NaOH in the hope that signals could be detected which were suitable for measuring the exchange by line broadening techniques. A very weak signal, probably peroxide was found in the perruthenate solution and no other signal was detected.

The exchange rate constant calculated from the equations of Marcus given in Section III-B of this thesis for a Ru-Ru distance of 5.61Å from crystalline potassium perruthenate (23) is $5 \times 10^2$ $\underline{M}^{-1}sec.^{-1}$ If we estimate that a water molecule intervenes between the oxygens of the two Ru-O units, $1.6 \times 10^7$ $\underline{M}^{-1}sec.^{-1}$ is calculated. The latter figure is more-or-less in agreement with the estimates from the experiments.