# The University of British Columbia

Faculty of Graduate Studies

PROGRAMME OF THE

# FINAL ORAL EXAMINATION
# FOR THE DEGREE OF
# DOCTOR OF PHILOSOPHY

*of*

## ARTHUR HUBERT WEBSTER

B.A. (Queen's University) 1953
M.A. (Queen's University) 1955

WEDNESDAY, APRIL 17, 1957, at 2:30 p.m.

IN THE PHYSICAL METALLURGY BUILDING
ROOM 204

### COMMITTEE IN CHARGE

DEAN G. M. SHRUM, *Chairman*

W. M. ARMSTRONG
W. A. BRYCE
J. DEUTSCH
F. A. FORWARD

J. HALPERN
C. REID
C. S. SAMIS
L. W. SHEMILT

*External Examiner*: PROFESSOR B. S. RABINOVITCH
University of Washington

# A KINETIC STUDY OF SOME HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN WITH METAL IONS IN AQUEOUS SOLUTION

## ABSTRACT

The kinetics of the silver ion catalysed reduction of dichromate by molecular hydrogen in aqueous solution were investigated over a wide range of conditions between 30 and 120°C. The rate was found to be independent of dichromate at sufficiently high concentrations of this oxidizing agent. The observed kinetics were consistent with the two simultaneous reaction paths,

(1) $H_2 + 2Ag^+ \rightarrow$ intermediates $\rightarrow$ products

giving third order kinetics; and,

(2) $H_2 + Ag^+ \leftrightarrows AgH + H^+$

$AgH + Ag^+ \rightarrow$ intermediates $\rightarrow$ products

The mechanism (1) predominated at low temperatures while the mechanism (2) accounted for most of the reaction at higher temperatures. Mechanism (2) was supported by experiments in which deuterium, added as $D_2O$ to the aqueous phase appeared as HD in the gas phase during the course of the reaction. As the dichromate concentration approached zero (at 110°C) the reaction assumed a high order in the $Ag^+$ concentration; this appears to reflect the aggregation of silver ions into incipient nuclei of metal particles.

The precipitation by hydrogen of silver metal from solutions of silver perchlorate, acetate and ethylene diamine was examined. The basic complexing agents accelerated the reaction, probably by stabilizing the protons released in the first step of reaction (2). The magnitude of the effect follows the order acetate, ethylene diamine, $H_2O$.

The reduction of permanganate by molecular hydrogen was studied over a wide pH range. The initial step,

$$H_2 + MnO_4^- \rightarrow MnO_4^{3-} + 2\,H^+$$

was proposed to account for the kinetics in both acidic and basic solutions. Silver perchlorate was found to act as a homogeneous catalyst for this reduction. The mechanism of the catalysed reaction may be,

$$Ag^+ + MnO_4^- \leftrightarrows AgMnO_4 \text{ (fast)}$$

$$AgMnO_4 + H_2 \rightarrow \text{intermediates} \rightarrow \text{products}$$

## PUBLICATIONS

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. I. (Low Temperature Catalytic Hydrogenation): A. H. Webster and J. Halpern, J. Phys. Chem., 60, 280-5 (1956).

Kinetics of the Reduction of Permanganate in Aqueous Solution by Molecular Hydrogen: A. H. Webster and J. Halpern, Trans. Faraday Soc., 53, 51-60 (1957).

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. II. (High Temperature Hydrogenation and Exchange Studies); A. H. Webster and J. Halpern, to be submitted to J. Phys. Chem.

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. III. (Precipitation of Metallic Silver from Solutions of Various Silver Salts): A. H. Webster and J. Halpern, to be submitted to J. Phys. Chem.

## GRADUATE STUDIES

Field of Study: Metallurgy

| | |
|---|---|
| Metallurgical Thermodynamics and Kinetics | C. S. Samis |
| Theory of Metal Reactions | J. Halpern |
| Structure of Metal Compounds | J. Halpern |
| Metal Surface Reactions | H. G. V. Evans |
| Theory of Alloys | H. P. Myers |

Other Studies:

| | |
|---|---|
| Theory of the Chemical Bond | C. Reid |
| Radiochemistry | M. Kirsch |
| Phase Transformations in Metals | W. M. Armstrong and J. G. Parr |
| Elementary Quantum Mechanics | G. M. Volkoff |
| Research Methods | H. P. Myers and J. G. Parr |

# A KINETIC STUDY OF SOME HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN WITH METAL IONS IN AQUEOUS SOLUTION

by

ARTHUR HUBERT WEBSTER

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in
METALLURGY

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
April, 1957

# ABSTRACT

The kinetics of the silver ion catalysed reduction of $Cr_2O_7^{=}$ by molecular hydrogen in aqueous solution were investigated over a wide range of conditions between 30° and 120°C. The rate was found to be independent of $Cr_2O_7^{=}$ at sufficiently high concentrations of this oxidizing agent. The observed kinetics were consistent with the existence of two simultaneous reaction paths,

$$(1) \quad H_2 + 2\,Ag^+ \xrightarrow{k_I} \text{intermediates} \longrightarrow \text{products},$$

giving third order kinetics, and,

$$(2) \quad H_2 + Ag^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AgH + H^+$$

$$AgH + Ag^+ \xrightarrow{k_2} \text{intermediates} \longrightarrow \text{products}.$$

The mechanism (1) predominated at low temperatures while the mechanism (2) accounted for most of the reaction at higher temperatures. Mechanism (2) was supported by experiments in which deuterium, added as $D_2O$ to the aqueous phase, appeared as HD in the gas phase during the course of the reaction. As the Cr(VI) concentration approached zero (at 110°C), the reaction assumed a high order in $Ag^+$ concentration; this appeared to reflect the aggregation of silver ions into incipient nuclei of metal particles.

The precipitation by hydrogen of silver metal from silver perchlorate, acetate, and ethylene diamine solutions was examined. The basic complexing agents accelerated the reaction, probably by stabilizing the proton released in the first step of reaction (2). The magnitude of the effect followed the order, acetate $>$ ethylene diamine $>$ $H_2O$.

Reduction of $MnO_4^-$ by molecular hydrogen was studied over a wide pH range. The initial step,

$$H_2 + MnO_4^- \longrightarrow MnO_4^{\equiv} + 2\ H^+$$

was proposed to account for the kinetics in both acid and basic solutions. Silver perchlorate was found to be a homogeneous catalyst for this reduction. The mechanism of the catalysed reaction may be,

$$Ag^+ + MnO_4^- \rightleftharpoons AgMnO_4 \qquad \text{(fast)}$$

$$AgMnO_4 + H_2 \longrightarrow \text{intermediates} \longrightarrow \text{products.}$$

# The University of British Columbia

Faculty of Graduate Studies

PROGRAMME OF THE

# FINAL ORAL EXAMINATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

*of*

## ARTHUR HUBERT WEBSTER

B.A. (Queen's University) 1953
M.A. (Queen's University) 1955

WEDNESDAY, APRIL 17, 1957, at 2:30 p.m.

IN THE PHYSICAL METALLURGY BUILDING
ROOM 204

COMMITTEE IN CHARGE

DEAN G. M. SHRUM, *Chairman*

| | |
|---|---|
| W. M. ARMSTRONG | J. HALPERN |
| W. A. BRYCE | C. REID |
| J. DEUTSCH | C. S. SAMIS |
| F. A. FORWARD | L. W. SHEMILT |

*External Examiner*: PROFESSOR B. S. RABINOVITCH
University of Washington

# A KINETIC STUDY OF SOME HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN WITH METAL IONS IN AQUEOUS SOLUTION

## ABSTRACT

The kinetics of the silver ion catalysed reduction of dichromate by molecular hydrogen in aqueous solution were investigated over a wide range of conditions between 30 and 120°C. The rate was found to be independent of dichromate at sufficiently high concentrations of this oxidizing agent. The observed kinetics were consistent with the two simultaneous reaction paths,

(1) $H_2 + 2Ag^+ \rightarrow \text{intermediates} \rightarrow \text{products}$

giving third order kinetics, and,

(2) $H_2 + Ag^+ \leftrightarrows AgH + H^+$

$AgH + Ag^+ \rightarrow \text{intermediates} \rightarrow \text{products}$

The mechanism (1) predominated at low temperatures while the mechanism (2) accounted for most of the reaction at higher temperatures. Mechanism (2) was supported by experiments in which deuterium, added as $D_2O$ to the aqueous phase appeared as HD in the gas phase during the course of the reaction. As the dichromate concentration approached zero (at 110°C) the reaction assumed a high order in the $Ag^+$ concentration; this appears to reflect the aggregation of silver ions into incipient nuclei of metal particles.

The precipitation by hydrogen of silver metal from solutions of silver perchlorate, acetate and ethylene diamine was examined. The basic complexing agents accelerated the reaction, probably by stabilizing the protons released in the first step of reaction (2). The magnitude of the effect follows the order acetate, ethylene diamine, $H_2O$.

The reduction of permanganate by molecular hydrogen was studied over a wide pH range. The initial step,

$$H_2 + MnO_4^- \rightarrow MnO_4^{2-} + 2H^+$$

was proposed to account for the kinetics in both acidic and basic solutions. Silver perchlorate was found to act as a homogeneous catalyst for this reduction. The mechanism of the catalysed reaction may be;

$$Ag^+ + MnO_4^- \leftrightarrows AgMnO_4 \text{ (fast)}$$

$$AgMnO_4 + H_2 \rightarrow \text{intermediates} \rightarrow \text{products}$$

# PUBLICATIONS

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. I. (Low Temperature Catalytic Hydrogenation): A. H. Webster and J. Halpern, **J. Phys. Chem.**, 60, 280-5 (1956).

Kinetics of the Reduction of Permanganate in Aqueous Solution by Molecular Hydrogen: A. H. Webster and J. Halpern, **Trans. Faraday Soc.**, 53, 51-60 (1957).

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. II. (High Temperature Hydrogenation and Exchange Studies); A. H. Webster and J. Halpern, to be submitted to J. Phys. Chem.

Homogeneous Catalytic Activation of Molecular Hydrogen in Aqueous Solution by Silver Salts. III. (Precipitation of Metallic Silver from Solutions of Various Silver Salts): A. H. Webster and J. Halpern, to be submitted to **J. Phys. Chem.**

## GRADUATE STUDIES

Field of Study: Metallurgy

| | |
|---|---|
| Metallurgical Thermodynamics and Kinetics | C. S. Samis |
| Theory of Metal Reactions | J. Halpern |
| Structure of Metal Compounds | J. Halpern |
| Metal Surface Reactions | H. G. V. Evans |
| Theory of Alloys | H. P. Myers |

Other Studies:

| | |
|---|---|
| Theory of the Chemical Bond | C. Reid |
| Radiochemistry | M. Kirsch |
| Phase Transformations in Metals | W. M. Armstrong and J. G. Parr |
| Elementary Quantum Mechanics | G. M. Volkoff |
| Research Methods | H. P. Myers and J. G. Parr |

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representative. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Mining and Metallurgy

The University of British Columbia,
Vancouver 8, Canada.

Date April 17, 1957

# ACKNOWLEDGMENTS

The author wishes to express his gratitude for the advice, help, and encouragement given by Dr. J. Halpern who directed this study, and to members of the staff of the Department of Mining and Metallurgy for their interest in this work.

The co-operation of Dr. D.J. Fabian and Dr. W.A. Bryce of the Department of Chemistry in performing the mass spectrometric analysis is greatly appreciated.

The author also wishes to thank the National Research Council for the award of a Studentship (1955-56) and Canadian Industries Limited for a Fellowship (1954-55).

# TABLE OF CONTENTS

Page

INTRODUCTION .. .. .. .. .. .. .. .. .. .. 1

GENERAL CONSIDERATIONS OF HYDROGENATION REACTIONS .. .. 1

HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN IN SOLUTION 5

PREVIOUS INVESTIGATIONS OF HYDROGENATIONS INVOLVING SILVER AND PERMANGANATE SALTS .. .. .. .. .. .. 10

OBJECT AND SCOPE OF THIS INVESTIGATION .. .. .. .. 11

PART I - THE HOMOGENEOUS ACTIVATION OF HYDROGEN BY SILVER SALTS 13

EXPERIMENTAL .. .. .. .. .. .. .. .. .. 13

MATERIALS .. .. .. .. .. .. .. .. .. 13

ANALYSIS .. .. .. .. .. .. .. .. .. 13

PROCEDURE .. .. .. .. .. .. .. .. .. 14

RESULTS AND DISCUSSION .. .. .. .. .. .. .. 20

A. SILVER ION CATALYSIS OF DICHROMATE REDUCTION .. 20

Low Temperature Results .. .. .. .. .. 22

High Temperature Results .. .. .. .. .. 35

Discussion .. .. .. .. .. .. .. .. 57

B. EXCHANGE EXPERIMENTS .. .. .. .. .. .. 68

C. SILVER PRECIPITATION FROM PERCHLORATE SOLUTION .. 74

D. SILVER PRECIPITATION FROM SOLUTIONS CONTAINING COMPLEXES OF SILVER .. .. .. .. .. .. 79

Acetate System .. .. .. .. .. .. .. 80

Ethylene Diamine System .. .. .. .. .. .. 84

PART II - REDUCTION OF PERMANGANATE BY MOLECULAR HYDROGEN .. 89

EXPERIMENTAL .. .. .. .. .. .. .. .. .. 89

RESULTS AND DISCUSSION .. .. .. .. .. .. .. 93

Reaction in Acid Solution .. .. .. .. .. .. 93

Page

Reaction in Neutral Solution .. .. .. .. .. 99

Reaction in Basic Solution .. .. .. .. .. .. 99

Effect of Added Salts on the Reaction in Acid Solution 104

Silver Ion Catalysed Reaction .. .. .. .. .. 106

Discussion of the Uncatalysed Reaction .. .. .. 113

Discussion of the Silver Catalysed Reaction .. .. 114

GENERAL DISCUSSION .. .. .. .. .. .. .. .. .. 118

REFERENCES .. .. .. .. .. .. .. .. .. .. 122

APPENDIX A - Summary of Experimental Results .. .. .. .. 127

APPENDIX B - Sample Calculation of Exchange Rate .. .. .. 137

APPENDIX C - Examination of Products Precipitated from Silver Solutions by Hydrogen .. .. .. .. .. 141

## TABLES

Table No. Page

I. Summary of homogeneous reactions of molecular hydrogen in organic solvents .. .. .. .. .. .. 6

II. Summary of homogeneous reactions of molecular hydrogen in aqueous solution .. .. .. .. .. .. 7

III. Relative reactivities of complexes of Cu(II) and of Hg(II) 8

IV. Rates of reaction of $H_2$ in the presence of $AgClO_4$ at 50°C. 23

V. Comparison of rates in autoclave and in glass apparatus 36

VI. Rates of reaction of hydrogen in the presence of $AgClO_4$ at 110°C .. .. .. .. .. .. .. .. 40

VII. Values of $k_{II}$ and $k'_{II}$ .. .. .. .. .. .. 48

VIII. Rates of reaction between $Cr_2O_7^=$ and $H_2$ at low $Cr_2O_7^=$ concentrations .. .. .. .. .. .. .. 54

IX. A comparison of some observed rates of reaction of $H_2$ in the presence of $AgClO_4$ with the corresponding calculated rates .. .. .. .. .. .. 60

X. A comparison of observed values of $K_0[H_2]$ and calculated values of $-d[H_2]/dt]_I$ .. .. .. .. .. 66

XI. Exchange experiments .. .. .. .. .. .. 71

XII. A comparison of observed rates of silver precipitation with rates calculated on the basis of results of Section A .. .. .. .. .. .. .. 75

XIII. Precipitation of silver by hydrogen from solutions of silver complexes .. .. .. .. .. .. 81

XIV. Reduction of permanganate by hydrogen in acid solution 94

XV. Rates of reduction of permanganate by hydrogen in neutral solution .. .. .. .. .. .. 100

XVI. Rates of reduction of permanganate by hydrogen in basic solution .. .. .. .. .. .. .. 100

XVII. Effect of various salts on the rate of reduction of permanganate by hydrogen in acid solution .. 105

XVIII. Kinetic data on the silver catalysed reduction of permanganate by hydrogen .. .. .. .. .. 107

XIX. Relative reactivities of complexes of Ag(I) .. .. 119

## FIGURES

Fig. No. Page

1. Apparatus for experiments at 30° to 70° .. .. .. 15
2. Stainless steel autoclave .. .. .. .. .. .. .. 18
3. Gas sampling system .. .. .. .. .. .. .. .. 19
4. Typical rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ at 50°C .. .. .. .. .. .. .. .. 24
5. Absorption spectra of $K_2Cr_2O_7$, $AgClO_4$, and a mixed solution of $K_2Cr_2O_7$ and $AgClO_4$ .. .. .. .. .. 26
6. Dependence of the rate on $H_2$ partial pressure at 49.6°C 27
7. Rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ in solutions containing different amounts of $AgClO_4$ at 50°C .. 29
8. Dependence of the rate on the concentration of $AgClO_4$ 30
9. Dependence of the rate on $[AgClO_4]^2$ .. .. .. .. 31
10. Dependence of the rate on $[AgNO_3]^2$ .. .. .. .. 32
11. Arrhenius plot showing the temperature dependence of $k_I$ 34
12. Rate plot for the reduction of $Cr_2O_7^=$ by $H_2$ at 69.7°C. Experiment carried out in autoclave .. .. .. 37
13. Typical rate plots of the reduction of $Cr_2O_7^=$ by $H_2$ at 110°C. .. .. .. .. .. .. .. .. 39
14. Effect of initial $Cr_2O_7^=$ concentration on the rate at 110°C. .. .. .. .. .. .. .. .. 41
15. Dependence of the rate on $H_2$ partial pressure at 110°C 42
16. Rate plots for the reduction of $Cr_2O_7^=$ with $H_2$ in solutions containing different amounts of $AgClO_4$ at 110°C. .. .. .. .. .. .. .. .. 43
17. Dependence of the rate on $AgClO_4$ concentration at 110°C 44
18. Dependence of the rate on $AgClO_4$ concentration; plotted according to equation (6) .. .. .. .. .. .. 46
19. Dependence of the rate on $HClO_4$ concentration; plotted according to equation (6) .. .. .. .. .. .. 47
20. Rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ at different temperatures .. .. .. .. .. .. .. .. 50

Fig. No. Page

21. Dependence of the rate on silver perchlorate concentration at different temperatures, plotted according to equation (6) .. .. .. .. .. .. .. 51

22. Plots of log $k_{II}$ and log $k'_{II}$ against 1/T .. .. 52

23. Typical rate plots for the reduction of dichromate by hydrogen at low dichromate concentrations .. .. 55

24. Rate plots for the reduction of $Cr_2O_7^=$ by hydrogen at 110°C in solutions containing different amounts of $AgClO_4$ (low dichromate concentration) .. .. 56

25. Dependence of log $\kappa_o$ on log $[AgClO_4]$ .. .. .. 58

26. Dependence of $1/\kappa_o$ on $HClO_4$ concentration .. .. 59

27. Deuterium exchange and reduction of $Cr_2O_7^=$ in $D_2O$ enriched solutions .. .. .. .. .. .. 72

28. Precipitation of silver from silver perchlorate solution. A plot of silver ion concentration against hydrogen ion concentration as determined at various times during the reaction .. .. .. 76

29. Rate plots for the precipitation of silver from perchlorate solution .. .. .. .. .. .. 77

30. Rate plot for dichromate reduction followed by silver precipitation .. .. .. .. .. .. .. 78

31. Rate plots for the precipitation of silver from acetate solutions by reduction with hydrogen .. .. .. 82

32. Effect of sodium acetate on the rate of precipitation of silver by hydrogen .. .. .. .. .. .. 83

33. Rate plots for the reduction of silver from solutions containing ethylene diamine .. .. .. .. 87

34. Effect of NaOH on the rate of precipitation of silver from silver-ethylene diamine complexes .. .. 88

35. Absorption spectra of a basic $KMnO_4$ solution before and after reduction by hydrogen .. .. .. .. 92

36. Typical rate plots for the reduction of permanganate by hydrogen in acid solution .. .. .. .. 95

37. Dependence of the rate of reduction of permanganate on $H_2$ pressure .. .. .. .. .. .. .. .. 96

Fig. No. Page

38. Arrhenius plot for the reduction of permanganate by hydrogen in 0.3 M. $HClO_4$ .. .. .. .. .. .. 97

39. Rate plots for the reduction of permanganate in 0.3 M. NaOH. Manganate and permanganate both determined 101

40. Rate plots for the reduction of permanganate by hydrogen in 0.3 M. NaOH. Total oxidizing capacity of the solutions determined; manganese assumed to be present as $MnO_4^-$ and $MnO_4^=$ only .. .. .. .. 102

41. Effect of acid and base on the rate of reduction of permanganate by hydrogen .. .. .. .. .. 103

42. Rate plots for the reduction of permanganate by hydrogen in the presence of $AgClO_4$ .. .. .. 108

43. Dependence of the rate of reduction of permanganate in the presence of $AgClO_4$ on hydrogen pressure 110

44. Dependence of k' on the concentration of AgClO4 .. 111

45. Arrhenius plot for the silver catalysed reduction of permanganate .. .. .. .. .. .. .. 112

46. Variation of $MnO_4^-$ absorption at 270 mμ with silver ion concentration .. .. .. .. .. .. 116

47. Potential energy diagrams for the reactions between silver ion and molecular hydrogen .. .. .. 120

48. Ratio of mass 3 peak / mass 2 peak plotted against mass 2 peak for ordinary hydrogen .. .. .. 140

49. Photomicrographs of precipitated silver .. .. 142

# A KINETIC STUDY OF SOME HOMOGENEOUS REACTIONS
# OF MOLECULAR HYDROGEN WITH METAL IONS
# IN AQUEOUS SOLUTION

## INTRODUCTION

### GENERAL CONSIDERATIONS OF HYDROGENATION REACTIONS

The investigation reported in this thesis forms part of a general kinetic study of the homogeneous reactions of molecular hydrogen with inorganic compounds in aqueous solution. This work has included investigations of the reactions of hydrogen with cupric, mercuric, and mercurous salts, and is here extended to salts of silver and of permanganate.

This extensive investigation of the reactions of hydrogen with inorganic substances was undertaken for three principal reasons: (1) the importance of hydrogen as a reducing agent in hydrometallurgy, (2) the similarities which might be expected to exist between the homogeneous and heterogeneous reactions of hydrogen, and (3) the importance of the reactions of hydrogen in the investigation of the principles governing the kinetics and mechanisms of chemical reactions in general.

In hydrometallurgy, reduction by hydrogen may be used to recover nickel, cobalt, and copper in metallic form from leach solutions containing salts of these metals (1, 2, 3). The precipitation of nickel and cobalt, after initiation by some nucleating agent, proceeds by heterogeneous catalysis on the surface of the metal particles present in the solution. The reaction between cupric salts and hydrogen has been shown to take place homogeneously, no nucleating agent being necessary to start the reaction (4). By careful control of solution composition and operating conditions, these metals may be selectively precipitated from mixed solutions (5). Further, the oxides of vanadium and uranium may be obtained in concentrated form by reduction of soluble compounds such as vanadate (6) and uranyl salts (7) to the insoluble oxides $V_2O_3$ and $UO_2$, respectively, in the presence of nickel powder which functions as a catalyst. In connection with reactions such as these, it seemed of interest to clarify the mechanisms by which hydrogen can react with inorganic salts in solution, and hence to establish the factors which affect the rates of these reactions. The study of the homogeneous reactions, in particular, would be useful, since their kinetics should be more amenable to interpretation than those of heterogeneous reactions.

Some parallelism between the homogeneous and heterogeneous reactions of hydrogen was anticipated on the assumption that both types of reaction involve the activation of hydrogen by the displacement of electrons from the hydrogen molecule to unfilled low-lying energy bands in the solids, or unfilled low energy orbitals in the ions in solution. The relationship between the two types of reactions has been discussed previously (8). For heterogeneous catalysts such as nickel, platinum, and palladium, the electrons from the hydrogen are believed to enter "holes" in the d bands of the metals (9, 10, 11). Support for this view is provided by the decrease in the paramagnetic susceptibility of such metals (which indicates the filling of the d bands) upon the adsorption of hydrogen (12), by the decrease in catalytic activity upon alloying the catalyst with a second metal of higher valence which donates electrons to fill the d bands (13, 14), and by the poisoning of the catalysts by strongly adsorbed electron donating molecules such as alkyl sulphides (15, 16). Very strong adsorption by a reactant or product in the catalysed reaction will also poison the catalyst (17). It has been pointed out (8) that the reactions of hydrogen with metal ions in solution also appear to involve displacement of electrons to vacant low energy levels, and that those ions which react with hydrogen are "isoelectronic" with atoms of the metals which, in the solid state, are catalysts for hydrogenation reactions. The decrease in reactivity of cupric and mercuric ions which takes place on complexing with ethylene diamine can be attributed to the filling of the electron accepting orbitals, just as poisoning by sulphides was attributed to the filling of the d band holes of heterogeneous catalysts.

The importance of the reactions of hydrogen in the general study of chemical kinetics and mechanisms lies principally in the relative simplicity of the hydrogen molecule. In hydrogenation processes difficulties due to side reactions and bond rearrangements will be minimized, and hence there will be a greater probability that the mechanism of the hydrogenation can be determined. Hydrogen can take part in chemical reactions under a variety of conditions and a number of different mechanisms have been developed to account for these reactions. In order to place the homogeneous hydrogenation reactions in their proper perspective a few examples of different types of reactions of hydrogen will be reviewed briefly.

In the gas phase, the reaction between $H_2$ and $Br_2$ (18) is governed by a chain mechanism involving H and Br atoms as chain carriers (19). Because of the high dissociation energy of the hydrogen molecule (103 kcal./mole) chain initiation by the thermal reaction, $H_2 \longrightarrow 2H$ is unlikely, thus in the $H_2$-$Br_2$ reaction, the chain initiation step is probably $Br_2 \rightarrow 2Br$, while in the homogeneous hydrogenation of ethylene (20) the first stage is believed to be

$$H_2 + C_2H_4 \longrightarrow H + C_2H_5^{\cdot} \quad ,$$

with an activation energy of about 60 or 70 kcal./mole (21, 22).

Molecular hydrogen may however be dissociated by collision with photo-excited atoms, for example,

$$Hg(^3P_1) + H_2 \longrightarrow 2\ H + Hg.$$

The H atoms so produced may then react with ethylene (23). On the other hand, as in the formation of HI from $H_2$ and $I_2$, reactions of hydrogen may involve a simple bimolecular mechanism. The chain mechanism does not compete with the direct reaction in this system (18) because of the high endothermicity (ca. 33 kcal./mole) of the step,

$$H_2 + I \longrightarrow HI + H.$$

The gas phase reactions of hydrogen, such as those mentioned above, usually proceed with quite high activation energies. However, on the surfaces of certain metals, hydrogen will react much more readily. For example, the apparent activation energy is 43 kcal./mole in the gas phase for the hydrogenation of ethylene, but only 11 kcal./mole on a nickel surface (25). Some aspects of this type of catalysis were discussed above. Certain semi-conductors (26) such as ZnO (27) and $Cr_2O_3$ (28, 29) also will catalyse hydrogenation reactions. In this connection it has been reported that an increase in the number of free electrons, in the case of ZnO (n-type), or decrease in the number of holes, in the case of $Cr_2O_3$ (p-type), increases the activity of the catalyst for $H_2$-$D_2$ exchange. The opposite would be expected if the activation involved the transfer of electrons from the hydrogen to the catalyst as was postulated for the transition metal catalysts. However, the adsorption of hydrogen at 300°C on p-type semi-conductors reduces conductivity, while adsorption on an n-type semi-conductor increases conductivity (30); this is as would be expected for the donation of electrons from the hydrogen to the oxide. The reasons for these conflicting indications in the case of semi-conducting catalysts are not understood.

Among the heterogeneous reactions of hydrogen on oxide surfaces are those in which the oxide itself is reduced (i.e. to a metal and water) (31, 32, 33). These reactions are generally autocatalytic, but attempts to relate their rates to the semi-conducting properties of the oxides have not been successful.

Hydrogen dissolved in a liquid can also undergo heterogeneous reaction on the surface of a solid catalyst, e.g. a transition metal. It can also be activated in solution by the enzyme hydrogenase (34, 35), which has been shown to catalyse the hydrogenation of fumarate, and the $H_2 - D_2$ exchange. Homogeneous activation of hydrogen may also be effected by certain metallic salts in aqueous or non-aqueous solution. The salt may itself be reduced or, alternatively, may catalyse the reduction of an otherwise inert substrate which is present in the solution. It is with such homogeneous reactions that the present study is concerned.

## HOMOGENEOUS REACTIONS OF MOLECULAR HYDROGEN IN SOLUTION

A number of systems in which hydrogen reacts homogeneously in a liquid phase (both aqueous and organic) have been described and studied kinetically. The hydrogen-activating species in these systems is generally a metal ion or a metal containing complex. The results of these kinetic investigations have been recently reviewed (36, 37) and are here summarized in Tables I and II. During the investigation of these reactions some effects of variation of solvent and of complexing agents have been studied; the relative rates obtained with various ligands attached to $Cu^{++}$ (57) and $Hg^{++}$ (61, 62) ions in aqueous solution are listed in Table III.

## TABLE I

Summary of homogeneous reactions of molecular hydrogen in organic solvents

| Hydrogenation Reaction | Catalyst | Solvent | Kinetics | $\Delta H^{\ddagger}$ kcal.mole$^{-1}$ | $\Delta S^{\ddagger}$ cal. deg.$^{-1}$mole$^{-1}$ | Temp. °C. | Proposed Mechanism | Refs. |
|---|---|---|---|---|---|---|---|---|
| $AgOAc \rightarrow Ag^0$ | - | pyridine | $k[H_2][AgOAc]$ | 12-14 | -25 | 25 to 78 | $AgOAc + H_2 \xrightarrow{k} AgH + HOAc$<br>$AgH + AgOAc \xrightarrow{fast} 2\ Ag + HOAc$ | (38)(39) |
| $Cu(OAc)_2 \rightarrow CuOAc$ | CuOAc | pyridine | $k[H_2][CuOAc]$ | | | 100 | $CuOAc + H_2 \xrightarrow{k} CuH + HOAc$<br>$CuH + 2Cu(OAc)_2 \xrightarrow{fast} 3CuOAc + HOAc$ | (38) |
| $Cu(OAc)_2 \rightarrow CuOAc$<br>p-benzoquinone $\rightarrow$ quinhydrone<br>o-p $H_2$ conversion<br>$D_2 \rightarrow HD$ | CuOAc | quinoline | $k[H_2][CuOAc]^2$ | 13-16 | -20 | 25 to 117 | $H_2 + 2Cu(I) \xrightarrow{k} 2Cu(I)H$<br>$Cu(I)H + Cu(II) \xrightarrow{fast} 2Cu(I) + H^+$<br>$Cu(I)H + substrate \xrightarrow{fast} products + Cu(I)$ | (40)(41)<br>(42)(43)<br>(44)(45) |
| $C_2H_4 + H_2 \rightarrow C_2H_6$ | $PtCl_2(C_2H_4)_2$ | acetone | | | | -30 to 0 | $2PtCl_2(C_2H_4)_2 + 2H_2 \rightarrow (PtCl_2C_2H_4)_2 + 2C_2H_6$<br>$(PtCl_2C_2H_4)_2 + 2C_2H_4 \rightarrow 2PtCl_2(C_2H_4)_2$ | (47) |
| Hydroformylation<br>Hydrogenation of α-β unsaturated carbonyl compounds | $Co_2(CO)_8$ | benzene, ether | $\frac{k_1k_3P_{H_2}[Co][X]}{k_3P_{H_2} + k_2\ P_{CO}}$ | | | 90 to 200 | $Co_2(CO)_8 + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7X + CO$<br>$Co_2(CO)_7X + H_2 \xrightarrow{k_3} Co_2(CO)_6 + HXCHO$<br>$Co_2(CO)_6 + 2CO \rightarrow Co_2(CO)_8$ | (48)(49)<br>(50)(51) |
| $D_2 \rightarrow HD$<br>o-p $H_2$ conversion | $NH_2^-$ | $NH_3$ | $k[NH_2^-][H_2]$ | | | -50 | $D_2 + NH_2^- \rightarrow D^- + DNH_2$<br>$D^- + HNH_2 \rightarrow HD + NH_2^-$ | (52) |

TABLE II

Summary of homogeneous reactions of molecular hydrogen in aqueous solution

| Hydrogenation Reaction | Catalyst | Kinetics | $\Delta H^{\ddagger}$ kcal.mole$^{-1}$ | $\Delta S^{\ddagger}$ cal.deg.$^{-1}$mole$^{-1}$ | Temp. °C | Proposed Mechanism | Refs. |
|---|---|---|---|---|---|---|---|
| $Cr(VI) \rightarrow Cr(III)$<br>$IO_3^- \rightarrow I_2$<br>$Ce(IV) \rightarrow Ce(III)$ | $Cu^{++}$ | $\frac{k_1[Cu^{++}]^2[H_2]}{(k_{-1}/k_2)[H^+]+[Cu^{++}]}$ | 26 | -10 | 80 to 140 | $Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+$<br>$CuH^+ + Cu^{++} \xrightarrow{k_2} 2Cu^+ + H^+$<br>$Cu^+ + \text{substrate} \xrightarrow{\text{fast}} Cu^{++} + \text{products}$ | (53) (54)<br>(55) |
| $Cr(VI) \rightarrow Cr(III)$<br>$2Cu(OAc)_2 \rightarrow Cu_2O$ | $Cu(OAc)_2$ | $k[Cu(OAc)_2][H_2]$ | 24 | -7 | 80 to 140 | $Cu(OAc)_2 + H_2 \xrightarrow{k} CuH^+ + HOAc + OAc^-$<br>$CuH^+ + Cu(II) \longrightarrow 2\ Cu(I) + H^+$ | (56) ( 58)<br>(59) |
| $2Hg^{++} \rightarrow Hg_2^{++}$ | - | $k[Hg^{++}][H_2]$ | 18 | -12 | 65 to 100 | $Hg^{++} + H_2 \xrightarrow{k} Hg + 2H^+$<br>$Hg + Hg^{++} \xrightarrow{\text{fast}} Hg_2^{++}$ | (8) (60) |
| $Hg_2^{++} \rightarrow 2Hg^{\circ}$ | - | $k[Hg_2^{++}][H_2]$ | 20 | -10 | 65 to 100 | $Hg_2^{++} + H_2 \xrightarrow{k} 2Hg + 2H^+$<br>$2\ Hg \xrightarrow{\text{fast}} 2\ Hg_{l}$ | (8) (60) |
| $MnO_4^- \rightarrow MnO_2$ | - | $k[MnO_4^-][H_2]$ | 16 | -12 | 6 to 25 | $MnO_4^- + H_2 \rightarrow MnO_4^{\equiv} + 2\ H^+$<br>$MnO_4^{\equiv} \xrightarrow{\text{fast}} MnO_2$ | (63) (64)<br>(65) |
| $Co(NH_3)_2^{++} \rightarrow Co^{\circ}$ | hydro-quinone | | | | | $H_2 + Q \rightleftharpoons QH_2$<br>$QH_2 + Co(NH_3)_2^{++} \rightarrow Q + Co + 2NH_4^+$ | (68) |
| $D_2 \rightarrow HD$<br>o-p $H_2$ conversion | $OH^-$ | $k[H_2][OH^-]$ | 23 | -7 | 80 to 110 | $D_2 + OH^- \rightarrow D^- + DOH$<br>$HOH + D^- \rightarrow OH^- + HD$ | (66) |

## TABLE III

Relative reactivities of complexes of Cu(II) and of Hg(II)

| Complexing Agent | $pK_A$ (a) | | Rate of activation of $H_2$ (relative to hydrated ion) | | N No. of ligands per complex | | $\frac{1}{N}\log K_{st}$ (b) | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | Cu(II) | Hg(II) | Cu(II) | Hg(II) | Cu(II) | Hg(II) |
| Ethylene Diamine | 7.2 | 10.0 | 0.1 | 0.001 | 2 | 2 | 10.01 | 11.71 |
| Glycine | 2.34 | 9.78 | $<0.5$ | - | 2 | - | 7.77 | - |
| Butyrate | 4.81 | - | 150 | - | 2 | - | - | - |
| Propionate | 4.87 | - | 150 | 0.04 | 2 | - | - | - |
| Acetate | 4.76 | - | 120 | 0.04 | 2 | 2 | 1.65 | 4.21 |
| Sulphate | - | 1.92 | 7 | 1.8 | 1 | 1 | 0.6 | 1.34 |
| Water | - | - | 1 | 1 | - | - | - | - |
| Bromide | - | - | - | 0.0017 | - | 2 | - | 7.54 |
| Chloride | - | - | 2.7 | 0.0025 | 4 | 2 | -1.15 | 6.61 |

(a) $pK_A = -\log \frac{[B][H^+]}{[BH^+]}$

(b) Stability constant, $K_{st} = \frac{[MB_n]}{[M][B]^n}$

References: (8), (57), (69), (70), (71), (76).

On the basis of their kinetic behaviour the homogeneous hydrogenation reactions involving copper, mercury, and silver ions may be classified into two types, i.e. those reactions in which two metal atoms participate in the activation process and those which involve only one metal atom. The activation of hydrogen by mercurous ions (60) in aqueous solution and cuprous acetate (40–45) in quinoline is of the former type, while reactions in which hydrogen is activated by mercuric (60) and cupric (54) ions in aqueous solution and by silver and cuprous acetates (38) in pyridine are of the latter type. It is likely that the initial activation process in some of these reactions involves the release of a proton, i.e.,

$$M^{+} + H_2 \longrightarrow MH + H^{+}.$$

The presence of a suitable base (which may be either a solvent molecule or a complexing agent) adjacent to the metal ion will tend to stabilize this proton and may thus accelerate the reaction and prevent possible back reactions (57, 61, 67). On the other hand, very strong complexing of the cation appears to inhibit the reaction; this may be due to filling of the low energy orbitals in the ion by electrons from the ligand.

Some of the other reactions listed in Tables I and II possess features of special interest. The reactions catalysed by ethylene platinous chloride (47) and dicobalt octacarbonyl (51) are the only ones which involve the hydrogenation of unsaturated C:C double bonds. The rate of the ethylene platinous chloride reaction appears to fall off sharply above -15°C. The deuterium exchange reactions observed in basic aqueous (66) and ammoniacal (52) solutions appear unique in that no metal ion is involved in the catalysis. It has been found, however, that hydroxyl ion will not catalyse hydrogen reductions in aqueous solution. The exchange reaction probably occurs by a mechanism involving synchronized proton transfer (66). Only a qualitative account (68) has been given of the reduction of cobaltous sulphate in the presence of hydroquinone. The permanganate reaction (63) appears to be the only reported case of the homogeneous uncatalysed reduction of an oxy-anion by hydrogen. A further investigation of this reaction is included in the present work.

## PREVIOUS INVESTIGATIONS OF HYDROGENATIONS INVOLVING SILVER AND PERMANGANATE SALTS

It has been known for many years (72) that hydrogen will precipitate silver from aqueous solutions of silver nitrate and ammoniacal silver chloride. No kinetic measurements on this system had been reported at the time that this investigation was undertaken. A few measurements reported recently (73) using silver sulphate solution suggest that the reaction, following an induction period, is first order in the silver salt and has an activation energy of about 20 kcal./mole. Qualitative observations have also been made (39) which indicate that silver is slowly precipitated by hydrogen at atmospheric pressure from aqueous solutions containing silver acetate and silver-pyridine complexes. The reduction of silver acetate in pyridine solution by hydrogen (39) was found to be first order in the concentration of Ag(I).

The ability of silver salts to promote the absorption of hydrogen by neutral aqueous permanganate solutions has been demonstrated (74, 75). A precipitate, reported to consist of $Ag_2Mn_2O_5$ and $Ag_2Mn_2O_4$, was formed which apparently catalysed heterogeneously the permanganate reduction reaction. The rate measurements, however, indicated that there was some contribution from a homogeneous reaction involving silver ion as a catalyst. Since it appeared that this catalytic effect was larger than that observed in the reduction of dichromate (vide infra), an investigation of this system was undertaken using acid solutions where complications due to heterogeneous catalytic contributions were minimized. Preliminary to this investigation, a kinetic study of the uncatalysed reduction of permanganate by hydrogen in acid solution was necessary. This reaction has been previously examined in some detail in neutral solution (63) where the kinetics were reported to be first order in permanganate concentration and first order in hydrogen pressure. Some early results have also been reported for acid and alkaline solutions (64, 65), but these were qualitative and of a contradictory nature.

## OBJECT AND SCOPE OF THIS INVESTIGATION

The kinetics of the homogeneous reactions of hydrogen in aqueous solution with cupric, mercuric, and mercurous ions, and some of their complexes have been previously investigated in detail, as reported above, and mechanisms for these reactions have been proposed. An extension of these investigations to the reaction of a simple univalent cation appeared desirable and silver salts, which were found to react with hydrogen at rates convenient for study and without undue complications, appeared to be a logical choice for this purpose. The first part of this thesis, therefore, describes a kinetic investigation of the activation of hydrogen in aqueous solution by silver salts (principally the perchlorate), as revealed by their catalytic effect on the reduction of dichromate, whose uncatalysed reaction with hydrogen is negligibly slow. Some of the details of the mechanism were elucidated by using an aqueous solvent enriched with $D_2O$ and measuring the rate of formation of HD. The kinetics of the precipitation of metallic silver from solutions of various silver salts by reduction with hydrogen were also examined, particularly to obtain information about the effect of complexing on the activation of hydrogen by silver ions.

The second part of this thesis relates to the homogeneous reduction of permanganate in aqueous solution by hydrogen. The kinetics of this reaction were investigated over a wider pH range than previously, and in addition, its catalysis by silver salts was examined in detail.

# PART I - THE HOMOGENEOUS ACTIVATION OF HYDROGEN BY SILVER SALTS

## EXPERIMENTAL

### MATERIALS

The perchlorate salts used in this investigation, $AgClO_4$, $NaClO_4$, and $Ce(ClO_4)_4$ were G.F. Smith Co. reagent grade products. Hydrogen and nitrogen gases were obtained from the Canadian Liquid Air Co. Ethylene diamine was Eastman Kodak "White Label" grade. The deuterium oxide (99.5%) was supplied by the Stuart Oxygen Co. All other chemicals were either Baker and Adamson or B.D.H. reagent grade products. In some experiments $AgClO_4$ and $NaClO_4$ solutions were prepared by neutralizing perchloric acid with silver oxide and sodium hydroxide, respectively. The experimental solutions were prepared by diluting aliquots of standardized stock solutions.

### ANALYSIS

Dichromate concentrations were determined spectrophotometrically at 350 mμ using a Beckman DU or DK-2 spectrophotometer. Changes in the extinction coefficient with acid concentration were determined experimentally; a small correction was applied to compensate for the absorption of the product Cr(III). Silver concentrations were determined by KCNS titration in acid solution using a ferric indicator. In reactions involving precipitation of silver the solutions were filtered before titration. When Ce(IV) was used in place of $Cr_2O_7^{=}$ as the reducible substrate, its concentration was found by the addition of excess standardized $FeSO_4$ and back titration with $Ce(HSO_4)_4$. In the determination of the acidity of solutions containing a high concentration of Cr(III) (from the reduction of $Cr_2O_7^=$), corrections were applied to compensate for acid consumed during the reduction and for base consumed by the precipitation of $Cr_2O_3$. Hydrogen - nitrogen gas mixtures were analysed by oxidation of the hydrogen over CuO.

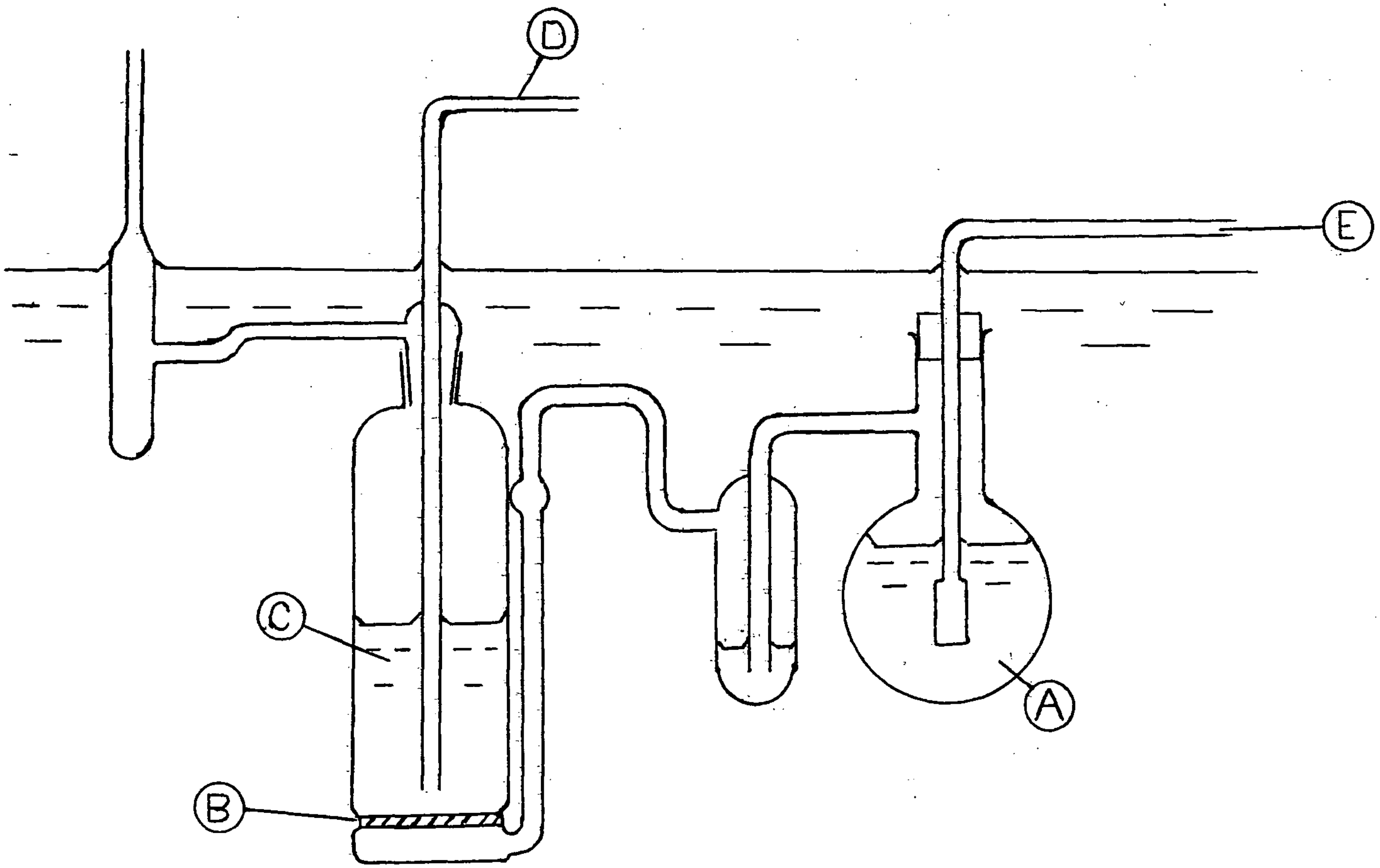
The deuterium content of the solvent used in the exchange experiments was determined by specific gravity measurements (77) before the addition of solutes. The concentration of the final solution was calculated, allowance being made for $H_2O$ added with the reagents. The $H_2$ - HD gas samples were analysed using a $90^o$ Nier type mass spectrometer*. The observed ratios of mass 3/mass 2 peaks were corrected for the contribution of the $H_3^+$ ions by subtracting the experimentally determined mass 3/mass 2 ratio for ordinary hydrogen. The variation of this ratio with ion current is shown in Appendix B.

PROCEDURE

For the low temperature investigations (30° to 70°C) the glass apparatus shown schematically in Fig. 1 was immersed in a water bath thermostated to ± 0.03°. The hydrogen gas was passed through a $NaNO_3$ solution to establish the required partial pressure of water vapour, and was then dispersed through a sintered glass plate into the reacting solution. It was determined that the hydrogen flow rate did not affect the observed reaction rate; hence it may be assumed that the solutions were saturated with hydrogen. After placing 250 ml. of the solution of the desired

---

* The mass spectrometric analyses were made by Dr. D. J. Fabian of the Department of Chemistry, U.B.C., whose assistance is gratefully acknowledged.



A NaNO$_3$ Solution
B Sintered Glass Plate
C Reacting Solution
D Sampling Tube
E H$_2$ Inlet

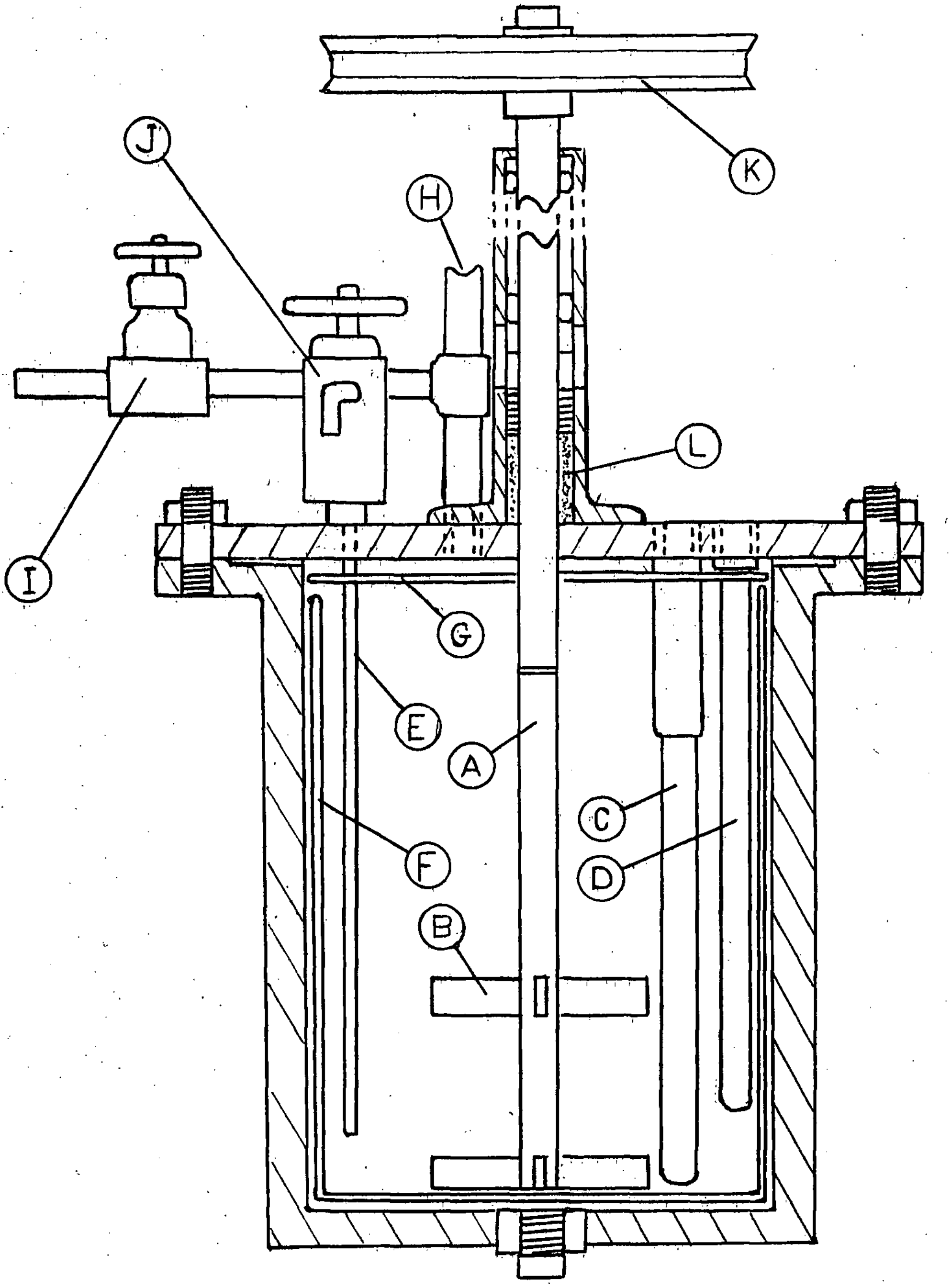
Fig. 1. Apparatus for Experiments at 30° to 70°C.

composition in the apparatus, the system was allowed to attain thermal equilibrium. The solution was sampled twice to determine its stability and then the hydrogen was introduced. The zero time was uncertain by the interval required to achieve saturation of the solution. The solution was sampled periodically and the samples were analysed as described previously. The partial pressure of hydrogen was determined by correcting the observed atmospheric pressure for the vapour pressure of the solution, estimated on the basis of recorded data for uni-uni valent electrolytes. Variation of the hydrogen partial pressure was achieved, when desired, by using analysed hydrogen - nitrogen mixtures.

For the high temperature studies a stainless steel autoclave fitted with a titanium liner, sampling tube, impeller, thermometer well, and thermoregulator well was used (Fig. 2). A teflon shield prevented splashing onto the roof of the autoclave. The apparatus was heated by an external gas burner. The temperature was controlled to ± 0.4° by means of a mercury thermoregulator which, through an electronic relay, activated a solenoid valve controlling the gas supply. The hydrogen pressure in the autoclave was controlled by a standard gas regulator and measured by a Bourdon type gauge; corrections were applied for the vapour pressure of the solution. The solution was stirred by an impeller of 3 inches diameter which was generally rotated at 900 r.p.m. It was ascertained that the observed reaction velocities were independent of the rate of stirring.

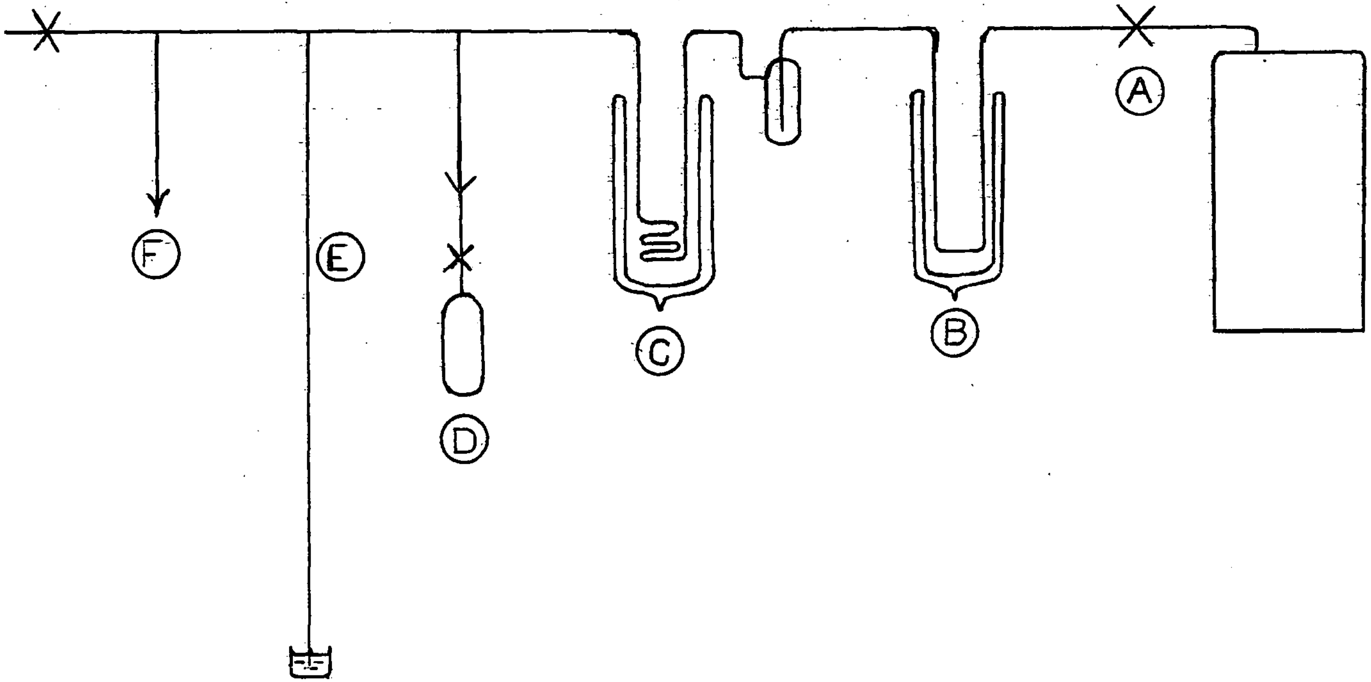
Three liters of solution of the desired composition were placed in the autoclave and heated to temperature under a nitrogen atmosphere. The solution was held under nitrogen, generally for 15 to 30 minutes, and sampled to determine its stability. After a thorough flushing with hydrogen, a constant pressure of hydrogen was maintained. The zero time of the reaction was uncertain by about four minutes, the time required for flushing. As in the case of the low temperature experiments the solution was periodically sampled and analysed.

Experiments were conducted using, as solvent, a mixture of deuterium and protium oxides with the object of following the appearance of HD in the gas phase. For this purpose a gas sampling train, shown in Fig. 3, was fitted to the exhaust valve of the autoclave. After release from the autoclave, the gas sample was passed into the evacuated train which contained ice and liquid air traps and a sample bulb of about 25 c.c. capacity. The gas samples were analysed mass spectrometrically as described previously. The general procedure for the deuterium exchange experiments was similar to that ordinarily used, except that no hydrogen was admitted to the apparatus after the commencement of the reduction. The dead volume of the system under the initial conditions of the experiments was determined as 1.74 liters.



| | | | |
|---|---|---|---|
| A | Impeller Shaft | G | Teflon Shield |
| B | Impeller Blade | H | Gas Inlet |
| C | Thermoregulator Well | I | Gas Exhaust Valve |
| D | Thermometer Well | J | Sampling Valve |
| E | Sampling Tube | K | Pulley |
| F | Titanium Liner | L | Packing Gland |

Fig. 2. Stainless Steel Autoclave.



A Exhaust Valve of Autoclave
B Ice Trap
C Liquid Air Trap
D Sample Bulb
E Manometer
F To Pump

Fig. 3. Gas Sampling System for Exchange Experiments.

## RESULTS AND DISCUSSION

### A. SILVER ION CATALYSIS OF THE REDUCTION OF DICHROMATE

In the presence of $AgClO_4$, $Cr_2O_7^{=}$ was found to react with $H_2$, over a wide range of conditions, according to the following stoichiometric relation,

$$Cr_2O_7^{=} + 3\ H_2 + 8\ H^+ \longrightarrow 2\ Cr^{+++} + 7\ H_2O \qquad \ldots\ldots\ (1).$$

In no case was there any indication of the formation of metallic silver until after the reduction of dichromate had gone to completion. Furthermore, no reduction of dichromate took place in the absence of the catalyst.

For convenience the formula $Cr_2O_7^{=}$ will be employed to denote all the Cr(VI) in solution. It is probable, however, that other forms of Cr(VI), in particular $HCrO_4^-$, are present and may in fact predominate (78). For most of the conditions under which the reaction was studied, the exact form of the Cr(VI) is not of importance. Also, since $Cr_2O_7^{=}$ does not generally enter into the rate determining step of the reaction, it is more appropriate, in accord with the usual convention, to formulate the rate law in terms of the rate of reaction of hydrogen (represented formally as $-d[H_2]/dt$). This rate of reaction is related to the measured rate of reduction of dichromate by the stoichiometry of equation (1), i.e.,

$$-\frac{d[H_2]}{dt} = -\frac{3\ d[Cr_2O_7^{=}]}{dt} \qquad \ldots\ldots\ (2).$$

The kinetics of the reaction (1) were studied under two sets of conditions, conveniently designated as "low temperature" and "high temperature"; the range of variables covered in the two regions of the investigation can be summarized as,

| | Low temperature region | High temperature region |
|---|---|---|
| Temperature | 30° - 70°C | 85° - 120°C |
| $AgClO_4$ | 0.02 - 0.11 M. | 0.005 - 0.028 M. |
| $HClO_4$ | 0.1 - 1.0 M. | 0.02 - 0.1 M. |
| Hydrogen Pressure | 0 - 0.9 atm. | 0 - 4 atm. |
| Temperature of most detailed study | 50°C | 110°C |

The general form of the kinetics in the low temperature region was quite different from the form in the high temperature region. An examination of the experimental results suggested a rate law of the form,

$$-\left.\frac{d[H_2]}{dt}\right]_I = k_I[Ag^+]^2[H_2] \qquad \ldots\ldots (3)$$

at low temperatures, and of the form,

$$-\left.\frac{d[H_2]}{dt}\right]_{II} = \frac{k_{II}[Ag^+]^2[H_2]}{k'_{II}[H^+] + [Ag^+]} \qquad \ldots\ldots (4)$$

at high temperatures. The rate law (3), it will be noted, is similar to the one proposed for the activation of hydrogen by CuOAc in quinoline, and the rate law (4) is similar to the one found for the activation of hydrogen by $Cu^{++}$ in perchloric acid solution. The two rate laws apparently apply to two independent processes which proceed simultaneously, and hence the total rate is given by,

$$-\frac{d[H_2]}{dt} = -\left.\frac{d[H_2]}{dt}\right]_I - \left.\frac{d[H_2]}{dt}\right]_{II} \qquad \ldots\ldots (5)$$

The experimental conditions in the two sections of the study were such that the path corresponding to rate (I) was favoured in the low temperature region, while that corresponding to rate (II) was favoured in the high temperature region.

The procedure followed in evaluating the constants in these equations was as follows,

1. An approximate Arrhenius expression for $k_I$ was calculated using the experimental results of the low temperature study.

2. The values of $k_I$ were calculated for the higher temperatures and the approximate values of $- d[H_2]/dt]_I$ were determined. These values were subtracted from the observed rates in this region to give an approximation of $- d[H_2]/dt]_{II}$ from which Arrhenius expressions for $k_{II}$ and $k'_{II}$ could be determined.

3. The values of $k_I$ and $k'_{II}$ were extrapolated to lower temperatures and used to calculate values of $- d[H_2]/dt]_{II}$ which could be applied as corrections to $- d[H_2]/dt$, giving a better approximation of $- d[H_2]/dt]_I$.

4. Steps 1. to 3. of this procedure were repeated to self consistency, i.e. until there was no further change in values of the constants $k_I$, $k_{II}$, and $k'_{II}$.

The detailed results will be considered in two parts, first for the low temperature region, and then for the high temperature region. In the discussion of the results a justification will be presented for the rate laws stated above.

## Low Temperature Results

A series of typical rate plots determined at 50°C is shown in Fig. 4. The rate of disappearance of $Cr_2O_7^=$ is seen to be essentially zero order with respect to the changing concentration of $Cr_2O_7^=$ and unaffected by variations in the initial concentration. Addition of $Cr(ClO_4)_3$ in amounts comparable to those formed during the reaction were also found to be without effect on the rate (see Table IV). A small induction

### TABLE IV

Rates of reaction of $H_2$ in the presence of $AgClO_4$ at 50°C.

| Temp. °C | Reactant × $10^4$ initial conc. M. | $HClO_4$ M. | $NaClO_4$ M. | $k_I \times 10^3$ $l.^2 mole^{-2} sec.^{-1}$ |
|---|---|---|---|---|
| 49.6 | 1.67 $K_2Cr_2O_7$ | 0.10 | 0.90 | 6.79 |
| 49.6 | 1.67 | 0.20 | 0.80 | 6.68 |
| 49.6 | 1.67 | 0.50 | 0.50 | 6.93 |
| 49.6 | 1.67 | 0.75 | 0.25 | 6.91 |
| 49.6 | 1.67 | 1.00 | 0.00 | 7.54 |
| 49.6 | 1.67 | 1.00 | 0.00 | 7.22 |
| 49.6 | 1.67 | 1.29 | 0.00 | 7.24 |
| 49.6 | 1.67 $K_2Cr_2O_7$ | 0.50 | 0.00 | 7.08 |
| 49.6 | 1.67 | 0.50 | 0.50 | 6.83 |
| 49.6 | 1.67 | 0.50 | 1.00 | 6.63 |
| 49.6 | 1.67 | 0.50 | 1.50 | 6.21 |
| 49.6 | 1.67 | 0.50 | 2.00 | 5.53 |
| 49.6 | 1.67 $K_2Cr_2O_7$ | 0.50 | 0.00 | 7.11 |
| 49.6 | 1.67 | 0.50 | 0.00 | 6.91 (a) |
| 50.0 | 0.67 $K_2Cr_2O_7$ | 0.50 | 0.00 | 6.96 (b) |
| 50.0 | 1.00 | 0.50 | 0.00 | 6.99 (c) |
| 50.0 | 1.33 | 0.50 | 0.00 | 7.10 (d) |
| 50.0 | 1.67 | 0.50 | 0.00 | 7.50 (e) |
| 50.0 | 1.20 $Ce(ClO_4)_4$ | 0.50 | 0.00 | 6.68 (f) |

(a) Reaction vessel packed with 2.2 grams of Pyrex glass wool.

(b) Hydrogen flow rate: 0.35 liter $min.^{-1}$

(c) " " " : 0.09 " "

(d) " " " : 0.21 " "

(e) Solution 2 × $10^{-4}$ M. in $Cr(ClO_4)_3$.

(f) Rate corrected for rate of decomposition of Ce(IV) in the presence of $AgClO_4$ without hydrogen, and also for a small apparent rate of reaction of Ce(IV) with hydrogen in absence of $AgClO_4$.

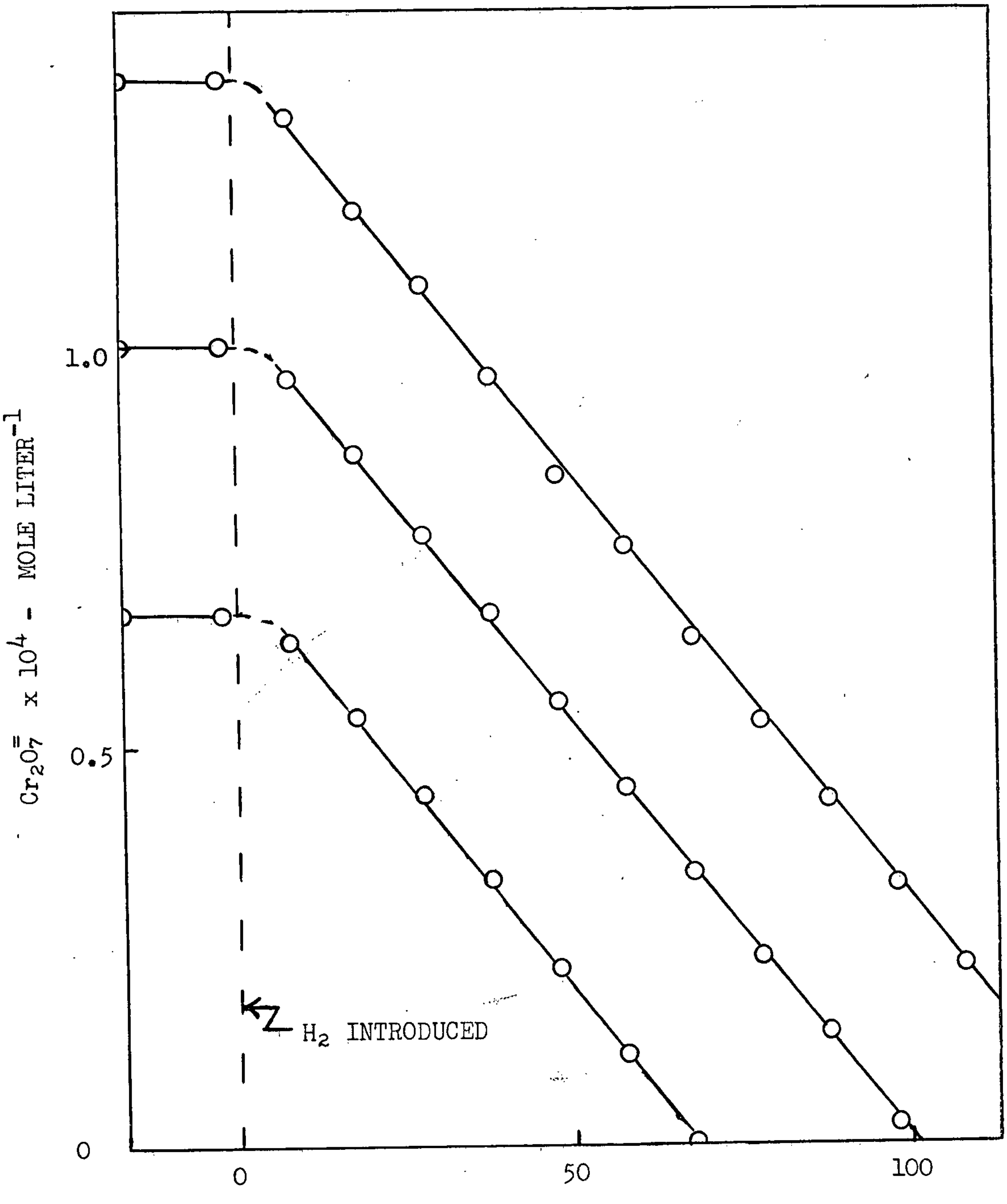


Fig. 4. Typical rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ at 50°C; 0.1 M. $AgClO_4$; 0.88 atm. $H_2$.

period was noted at the commencement of most of the reactions, before the final zero order rate was attained. This may be an apparent effect due to the presence in the solution of a trace amount of an impurity which reduces preferentially to $Cr_2O_7^=$. For example, it is estimated that less than $10^{-5}$ M. $ClO_3^-$ could account for the observed effect. It may be concluded that $Cr_2O_7^=$ does not participate in the rate determining step although its reduction serves as a convenient measure of the rate of reaction of hydrogen in solution. Values of $-\ d[H_2]/dt$ were calculated from the measured zero order rate of disappearance of $Cr_2O_7^=$ and were generally reproducible to within ± 5%.

Evidence for the absence of any large degree of interaction, such as complex formation between $Ag^+$ and $Cr_2O_7^=$ in solution, is provided by the observation that the absorption spectra of $Cr_2O_7^=$ and $Ag^+$ are almost additive, as shown in Fig. 5.

The suggestion that $Cr_2O_7^=$ does not take part in the rate determining step receives support from the result of an experiment (Table IV) in which $Ce^{++++}$ was substituted for $Cr_2O_7^=$ as the reaction substrate. Within the experimental error involved in the comparison, the rate of reaction of hydrogen calculated from the zero order rate of reaction of $Ce^{++++}$, is the same as that determined using $Cr_2O_7^=$.

Evidence for the homogeneous character of the reaction is provided by the results of another experiment (see Table IV) in which the reaction vessel was packed with 2.2 grams of Pyrex glass wool. The rate was the same as in the unpacked vessel.

Figure 6* shows the rate of reaction to be directly proportional to

---

* The data for the figures in the text are tabulated in Appendix A.

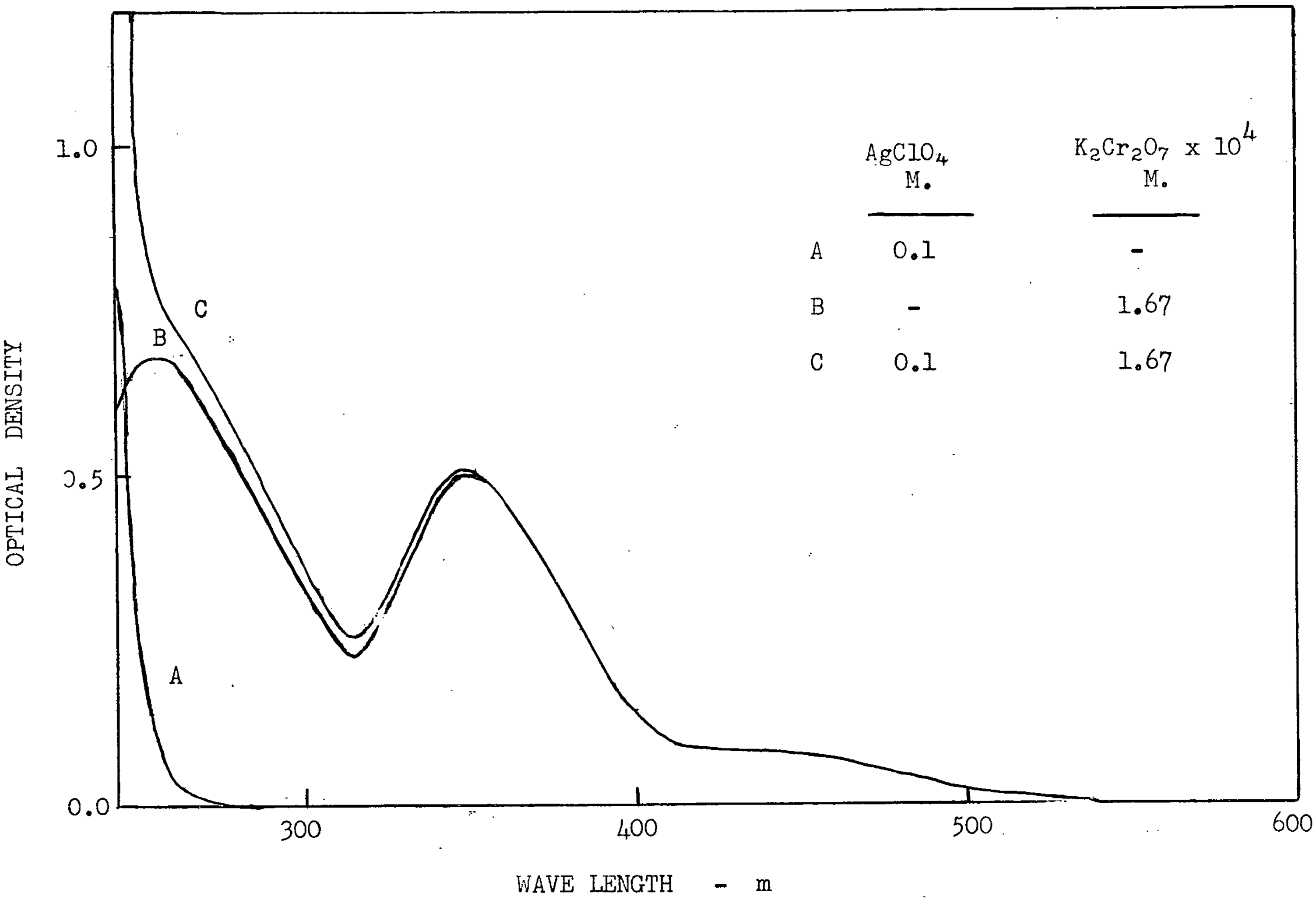


Fig. 5. Absorption spectra of $K_2Cr_2O_7$, $AgClO_4$, and a mixed solution of $K_2Cr_2O_7$ and $AgClO_4$. Solutions 0.5 M. $HClO_4$.

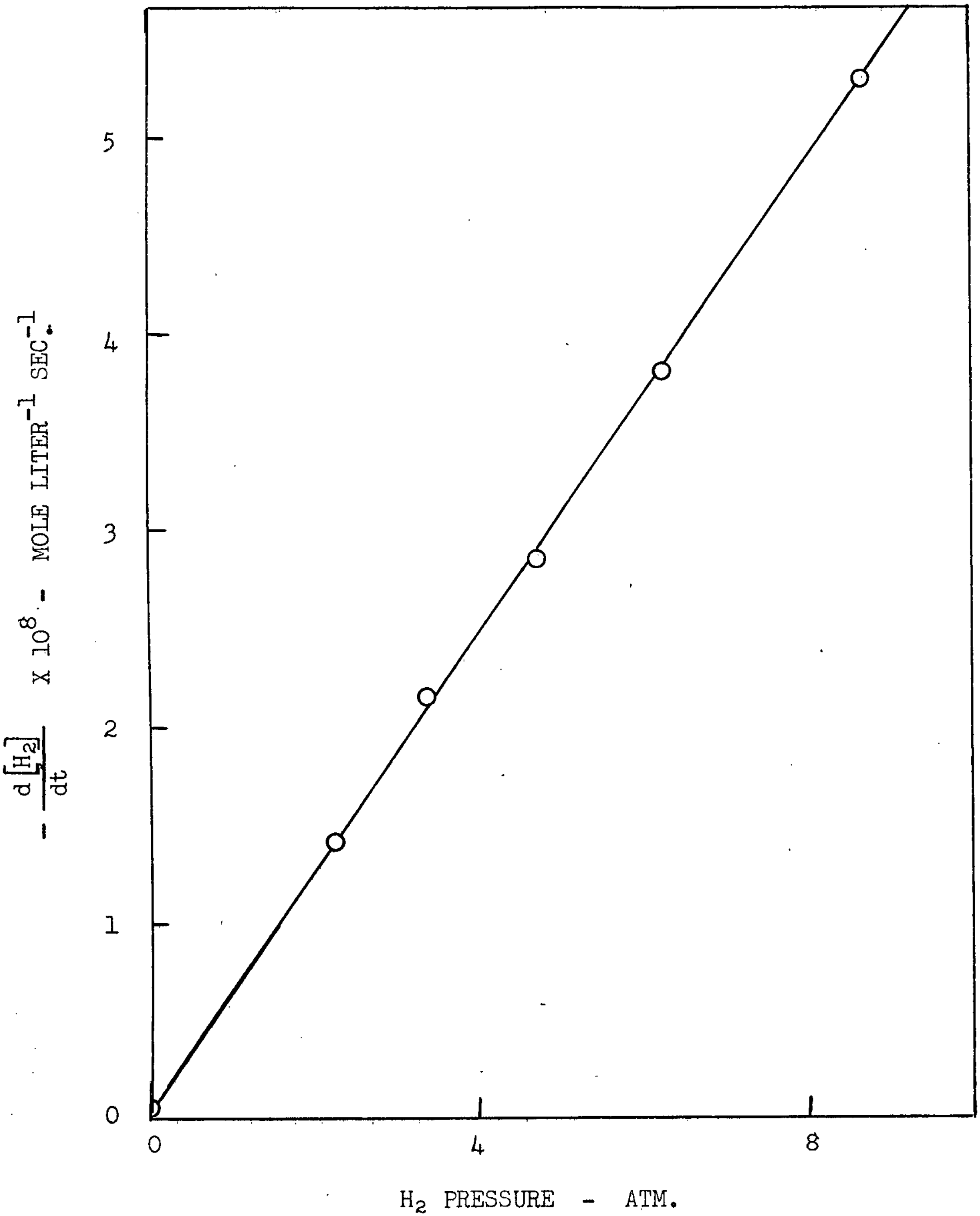


Fig. 6. Dependence of the rate on $H_2$ partial pressure at 49.6°C ; 0.5 M. $HClO_4$ ; 0.1 M. $AgClO_4$.

the partial pressure of hydrogen. Since the solubility of hydrogen in water in this region obeys Henry's law (79) it may also be concluded that the rate is proportional to the concentration of hydrogen in solution, $[H_2]$. Wiebe and Gaddy's data (80) for the solubility of hydrogen in water were used for the evaluation of rate constants expressed in concentration units. The small effect of the electrolytes on the solubility of hydrogen was neglected in the absence of data for solutions of the compositions employed in this investigation.

The catalytic influence of $Ag^+$ on the reaction is clearly demonstrated in Fig. 7 which shows rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ in solutions containing various amounts of $AgClO_4$. No reaction could be detected in the absence of $Ag^+$, while progressively higher rates were obtained as the $Ag^+$ concentration was increased up to 0.108 M. The nature of the dependence is shown more explicitly in Fig. 8, where the reaction rates determined at 40°, 50°, and 70°C are plotted as functions of the silver concentration. In Fig. 9 these rates are replotted as functions of the square of the silver concentration. At each temperature it is observed that the results conform approximately to a second order plot, the rate being roughly proportional to $[Ag^+]^2$. Detailed inspection reveals a deviation from this relation in the direction of lower order, reflected in the fact that the plots of rate against $[Ag^+]^2$ are not exactly linear. However, when the finally determined values of $-\,d[H_2]/dt]_{II}$ are subtracted from the observed rates to give $-\,d[H_2]/dt]_I$, these deviations are removed, as the plots, also shown in Fig. 9, demonstrate.

Results similar to those reported above were obtained in a series of experiments at 50°C in which nitrate was substituted for perchlorate. The slope of the nearly linear plot of rate against $[AgNO_3]^2$ shown in Fig. 10,

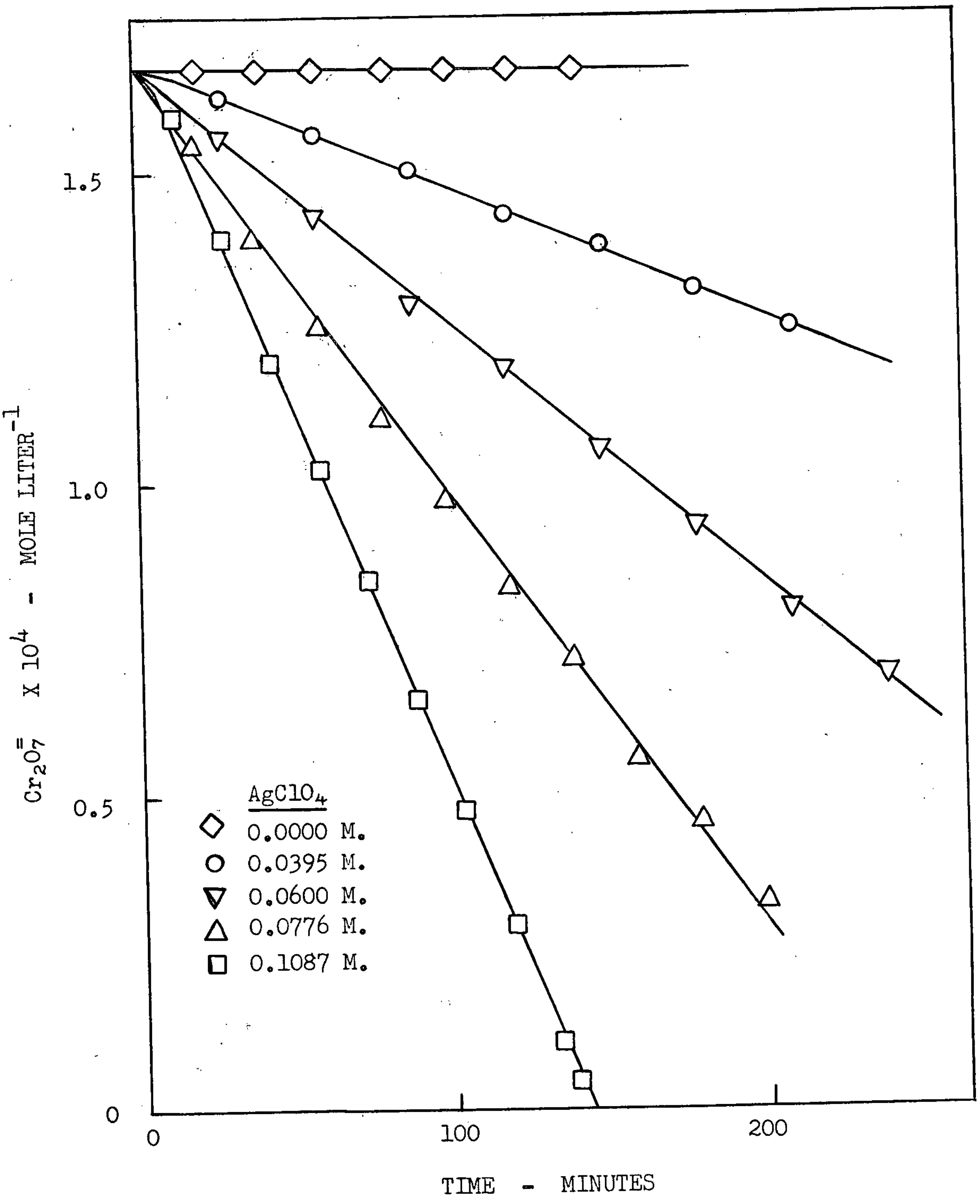


Fig. 7. Rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ in solutions containing different amounts of $AgClO_4$; Temp. 50°C. $H_2$ pressure, 0.88 atm.; Solutions 0.5 M. $HClO_4$.

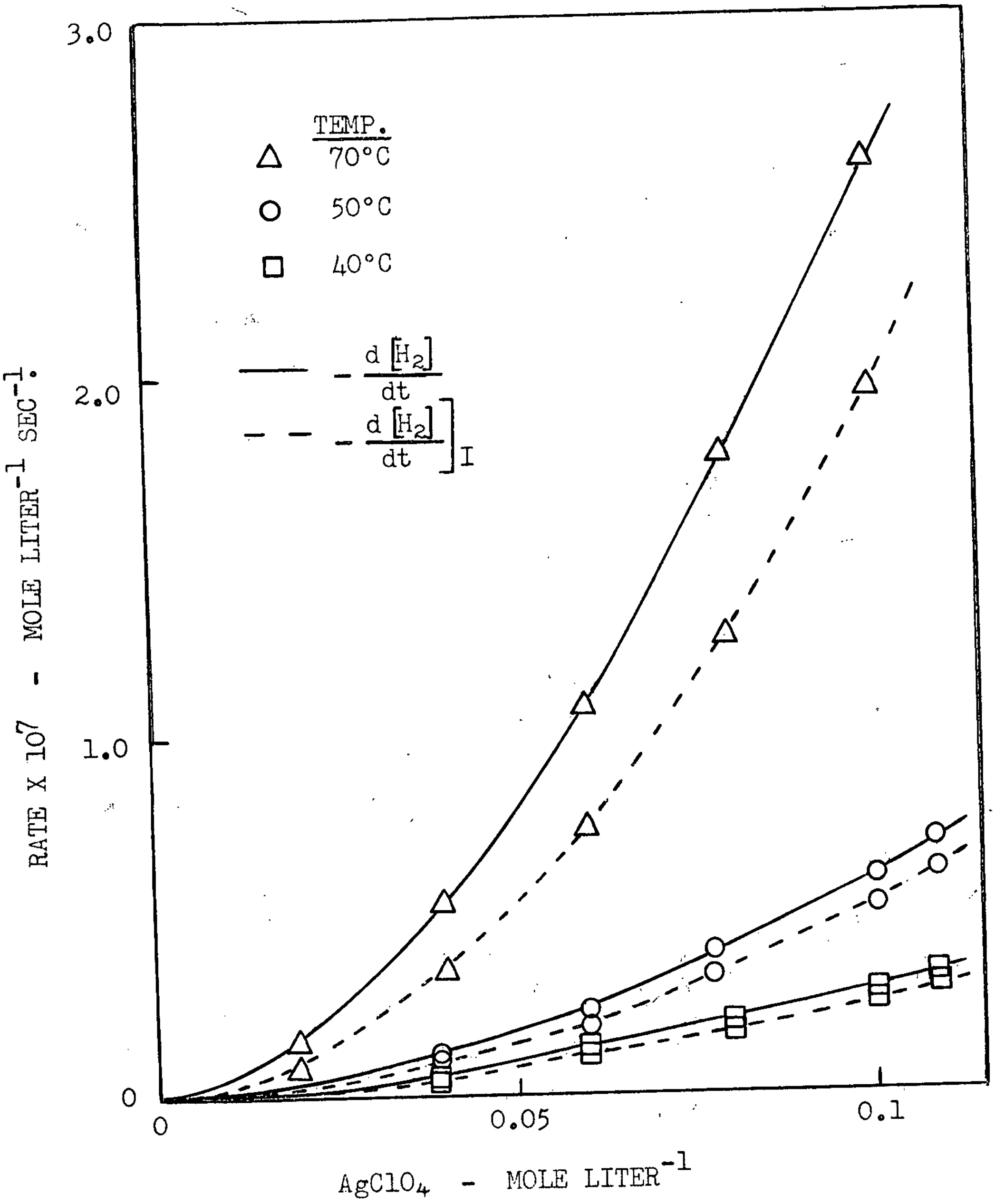


Fig. 8. Dependence of the rate on the concentration of $AgClO_4$. Solutions 0.5 M. $HClO_4$; all rates converted to 1 atm. $H_2$.

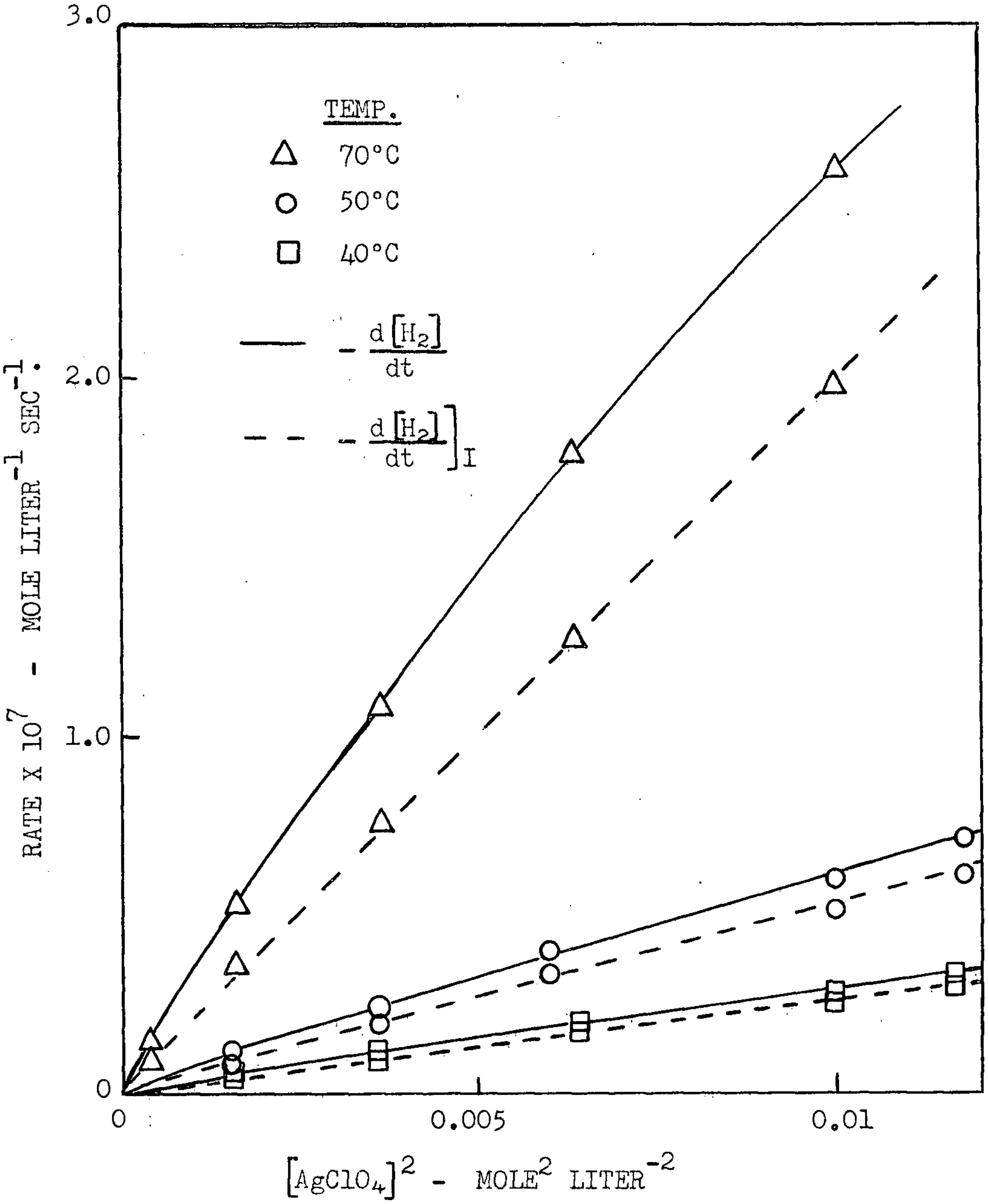


Fig. 9. Dependence of the rate on $[AgClO_4]^2$. Solutions 0.5 M. $HClO_4$; all rates converted to 1 atm. $H_2$.

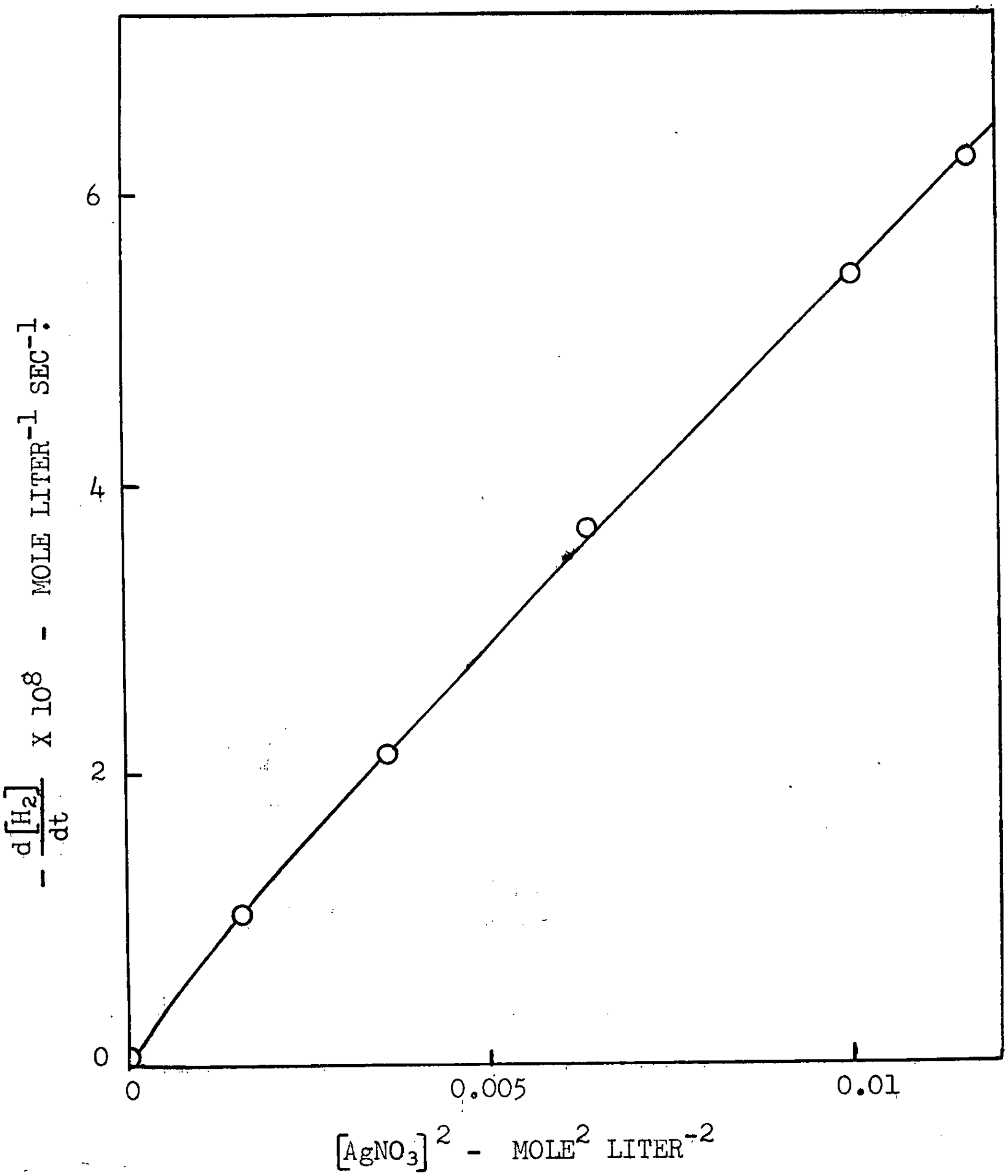


Fig. 10. Dependence of the rate on $[AgNO_3]^2$. Solutions 0.5 M. $HNO_3$; all rates converted to 1 atm. $H_2$, assuming rate $\propto P_{H_2}$ for the nitrate system.

is about 10% lower than that for comparable perchlorate solutions, possibly the result of some complexing between $Ag^+$ and $NO_3^-$ or the influence of a small salt effect on the reaction or on the solubility of $H_2$.

The results listed in Table IV show that essentially no effect on the rate was observed when $HClO_4$ concentration was varied between 0.1 and 1.0 M. (the total ionic strength being held constant at 1.1 by simultaneous variation of the $NaClO_4$ concentration). Also a negligible effect was observed when the $NaClO_4$ concentration was varied between zero and 1.0 M. in the presence of constant concentrations of 0.1 M. $AgClO_4$ and 0.5 M. $HClO_4$. At higher $NaClO_4$ concentrations (1.5 - 2.0 M.) a slight decrease in the rate was noted. Unfortunately no measurements of the salt effect could be made in solutions of much lower ionic strength (i.e. $<0.1$) because of the need to maintain critical minimum concentrations of both $AgClO_4$ and $HClO_4$ in the solution in order to obtain measurable reaction rates and to prevent the precipitation of the slightly soluble silver chromate.

The rates measured at five different temperatures from 30° to 70°C gave the Arrhenius plot shown in Fig. 11. From the slope of this plot an apparent activation energy of 14.7 ± 0.5 kcal./mole was calculated.

From the results presented above it may be concluded that the relationship given by equation (3) adequately describes the kinetics of the reaction in the low temperature region, after corrections have been applied for the contribution of $-\,d[H_2]/dt]_{II}$. The expression for $k_I$ was found to be,

$$k_I = 6.8 \times 10^7 \exp\,[-\,14.7 \times 10^3/\,RT] \text{ liter mole}^{-1}\text{ sec}^{-1}.$$

The corresponding values of the entropy and enthalpy of activation are $\Delta S^{\ddagger} = -\,25 \pm 2$ cal. deg.$^{-1}$ mole$^{-1}$ and $\Delta H^{\ddagger} = 14.1 \pm 0.5$ kcal. mole$^{-1}$,

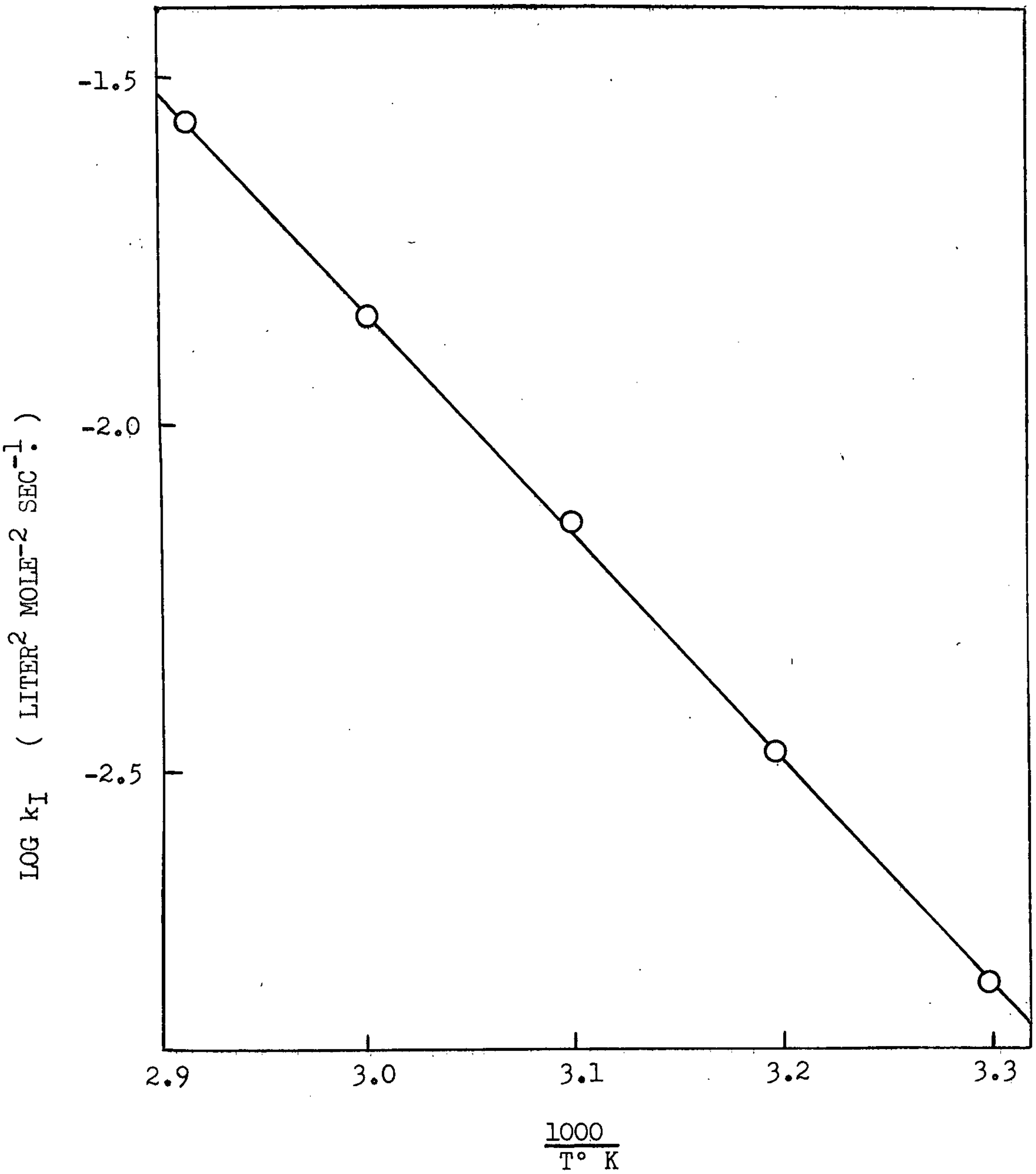


Fig. 11. Arrhenius plot showing the temperature dependence of $k_I$. Solutions 0.5 M. $HClO_4$; 0.10 M. $AgClO_4$.

the standard states being hypothetical 1 mole liter$^{-1}$ (activity coefficients neglected).

## High Temperature Results

Kinetic measurements obtained from autoclave experiments are compared in Table V with measurements made in the glass apparatus at 70°C. The results are of the same form as those found in the glass apparatus (see Fig. 12) but the measured rates appear to be about 12% lower; this small discrepancy might be due to any of a number of factors relating to the difference in the procedures used, e.g. small errors in the absolute temperature and pressure measurements. In this connection it should be noted that the conditions under which the comparison is made are close to the extreme limits of applicability of both procedures. Both measurements are therefore subject to maximum experimental error.

The typical rate plots for the reduction of dichromate at 110°C, shown in Fig. 13, differ from those obtained at the low temperatures, in that at low $Cr_2O_7^=$ concentrations the rates are no longer zero order in $Cr_2O_7^=$, but show a positive dependence on the $Cr_2O_7^=$ concentration.

The investigation of the kinetics in the high temperature region may therefore be divided into two parts, the first concerned with the region in which the rate is independent of the $Cr_2O_7^=$ concentration, and the second with the region of low $Cr_2O_7^=$ concentrations. Experimentally the two regions were investigated separately. The zero order rates, which are more easily interpreted, will be considered first.

### (i) High dichromate concentration

From the slopes of the initial linear portions of the rate plots

## TABLE V

Comparison of rates in autoclave and in glass apparatus

Initial $Cr_2O_7^=$ concentration, 1.67 $10^{-4}$ M.

$HClO_4$ concentration, 0.5 M.

| Apparatus | $AgClO_4$ M. | $H_2$ Pressure atm. | Temp. °C | $-d[H_2]/dt$ mole $l.^{-1}sec.^{-1}$ | $-d[H_2]/dt$ mole $l.^{-1}sec.^{-1}$ |
|---|---|---|---|---|---|
| glass | 0.0402 | 0.705 | 70.0 | $3.64 \times 10^{-8}$ | $1.79 \times 10^{-7}$ * |
| autoclave | 0.0381 | 4.0 | 69.7 | $1.59 \times 10^{-7}$ | $1.59 \times 10^{-7}$ |
| autoclave | 0.0389 | 4.0 | 69.7 | $1.67 \times 10^{-7}$ | ($1.60 \times 10^{-7}$) |

* Rate converted to 4.0 atm. $H_2$; 69.7°C; 0.0381 M. $AgClO_4$ on the basis of kinetics previously determined.

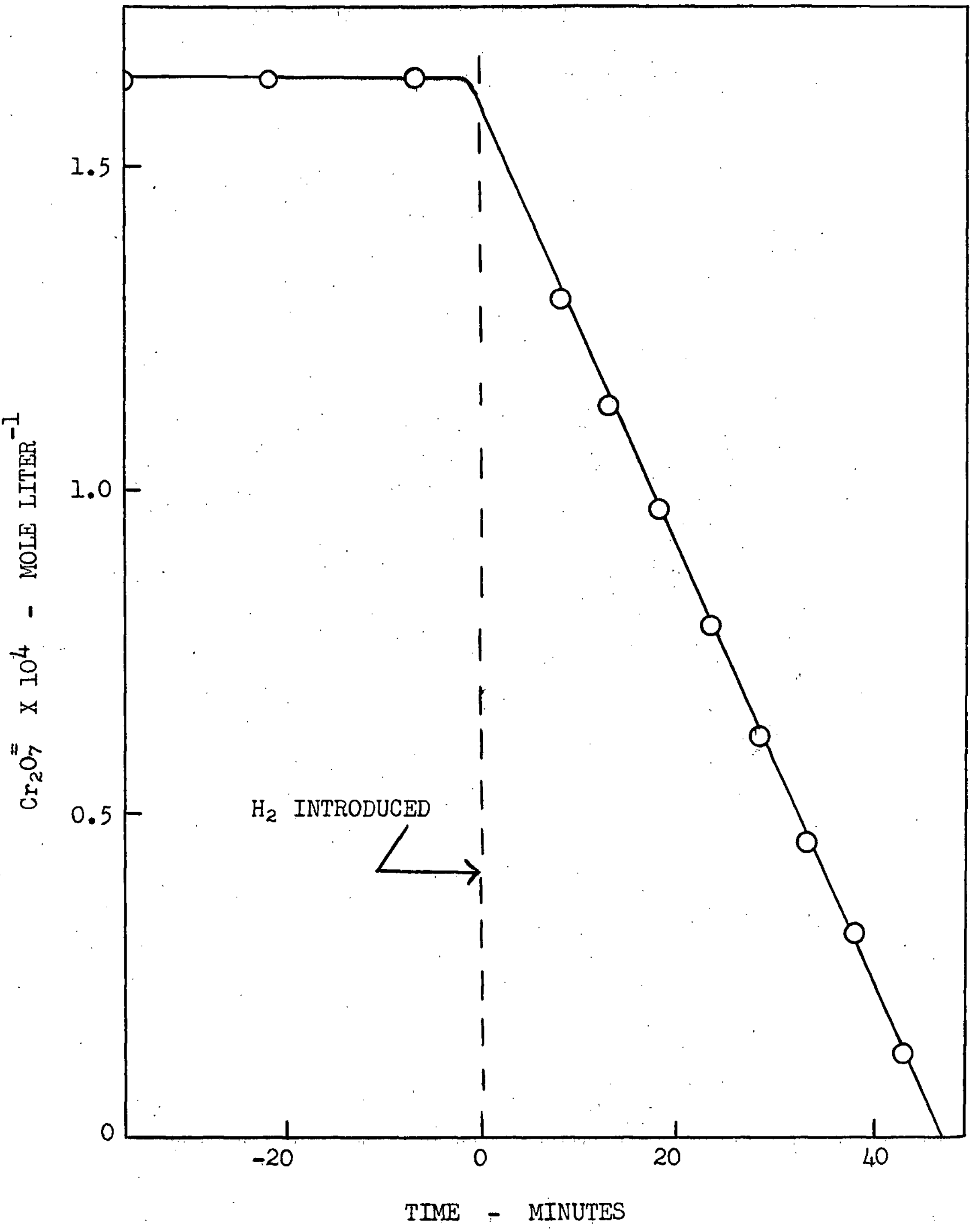


Fig. 12. Rate plot for the reduction of $Cr_2O_7^=$ by $H_2$ at 69.7°C. Experiment carried out in autoclave (cf. Fig. 4 for rate plots determined using glass apparatus). Solution 0.0389 M. $AgClO_4$; $H_2$ pressure, 4.0 atm.

shown in Fig. 13 the rates of reduction of $Cr_2O_7^=$ by hydrogen can be calculated. These observed rates were expressed in terms of $- d[H_2]/dt$ as discussed previously. The results presented in Table VI indicate that the rates increase as the initial dichromate concentration is raised. It appears, however, that a limiting rate is approached, as may be seen by reference to Fig. 14, in which the variation of the rate is plotted against initial $Cr_2O_7^=$ concentration. An endeavour was made to conduct the experiments under conditions such that the observed rates were close to this limiting rate. Solutions initially 2.5 X $10^{-3}$ M. in $Cr_2O_7^=$ were generally employed, this upper limit of the concentration being fixed by the solubility of silver chromate. From Fig. 14 it may be estimated that errors due to failure to attain the limiting rate may be about 10%.

Fig. 15 shows the rate of the reaction to be directly proportional to the partial pressure of hydrogen at 110°C, in agreement with observations reported for 50°C. It may be concluded, as in the low temperature investigation, that the rate is also proportional to the concentration of $H_2$ in solution; this concentration was calculated as described earlier.*

The rate curves plotted in Fig. 16 indicate the effect of $AgClO_4$ on the reaction at 110°C. When the rates determined from the linear portions of these curves are plotted (Fig. 17), the dependence of $- d[H_2]/dt$ on $AgClO_4$ concentration is shown more clearly. From a comparison of the results for solutions 0.03 and 0.1 M. in $HClO_4$, it is apparent that the acid concentration has a large effect on the observed

---

* Extrapolation of Wiebe and Gaddy's values (80) gave Bunsen absorption coefficients of 0.0188 and 0.0198 at 110° and 120°, respectively.

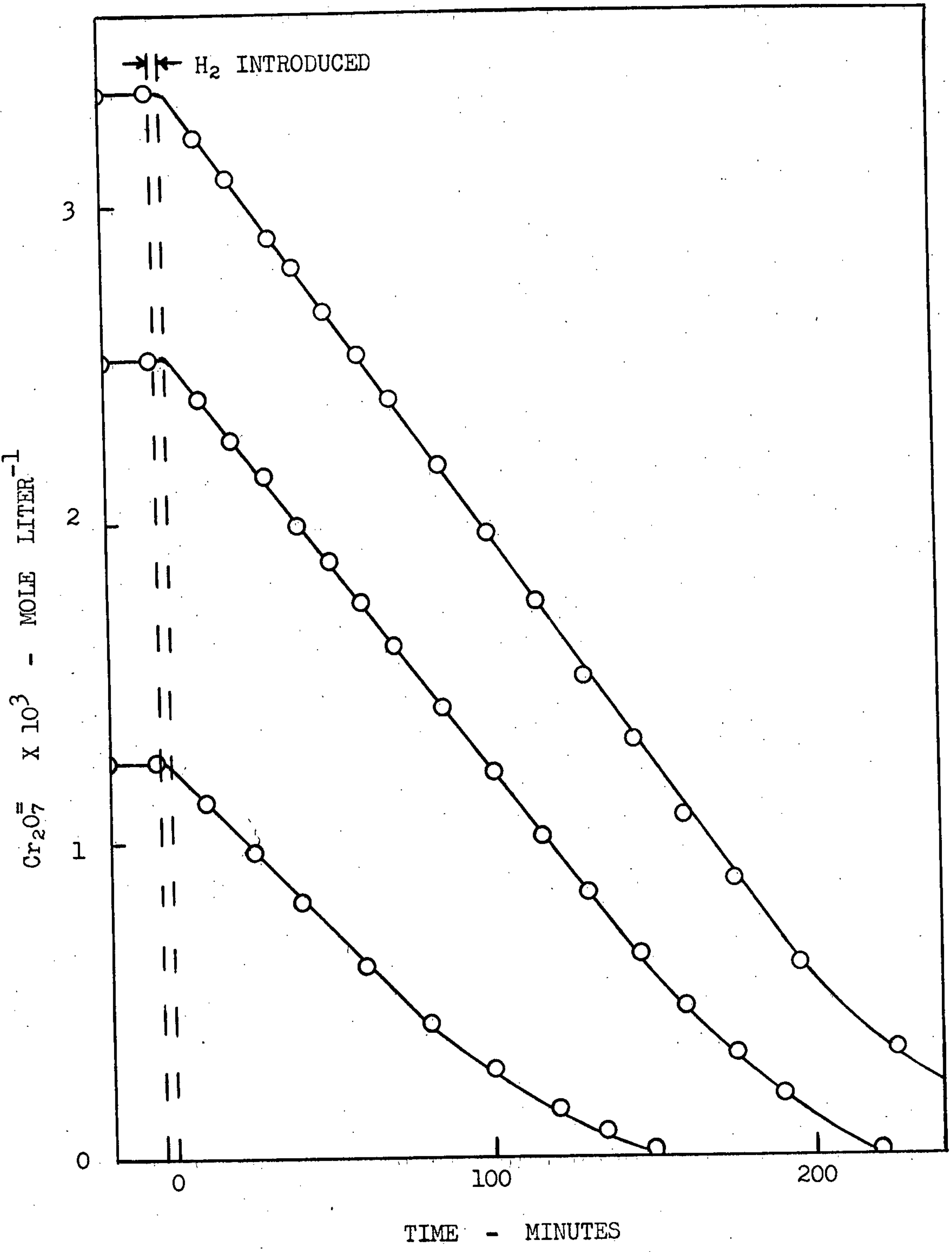


Fig. 13. Typical rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ at 110°C. Solutions $9.6 \times 10^{-3}$ M. $AgClO_4$; $3.1 \times 10^{-2}$ M. $HClO_4$; $H_2$ pressure, 4.0 atm.

## TABLE VI

Rates of reaction of hydrogen in the presence of $AgClO_4$ at 110°C, as determined from the initial linear portions of the rate plots.

$H_2$ Pressure, 4.0 atm.

| Initial $Cr_2O_7^{=} \times 10^3$ M. | $AgClO_4 \times 10^3$ M. | $HClO_4 \times 10^2$ M.(a) | $-d[H_2]/dt \times 10^7$ mole l.$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|
| 1.25 | 9.5 | 3.0 | 5.4 |
| 2.50 | 9.6 | 3.1 | 6.5 |
| 3.33 | 9.6 | 3.2 | 6.9 |
| 2.50 | 9.5 | 3.0 | 5.8 (b) |
| 2.50 | 10.0 | 10.1 | 3.5 (c) |
| 2.50 | 9.9 | 10.4 | 3.6 (d) |

(a) Initial concentration; acid is consumed during the reaction according to equation (1).

(b) Solution 0.27 M. in $NaClO_4$.

(c) Impeller rotated at 900 r.p.m.

(d) " " " 750 r.p.m.

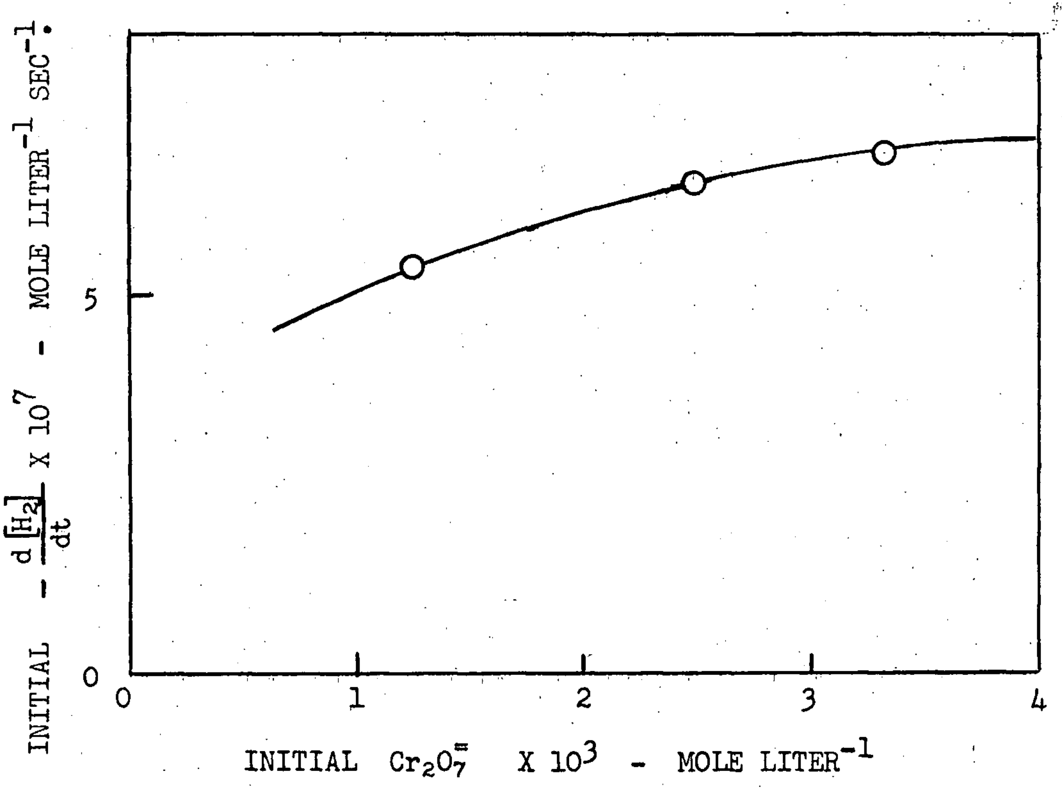


Fig. 14. Effect of initial $Cr_2O_7^=$ concentration on the rate at 110°C as determined from the initial linear portions of the plots in Fig. 13.

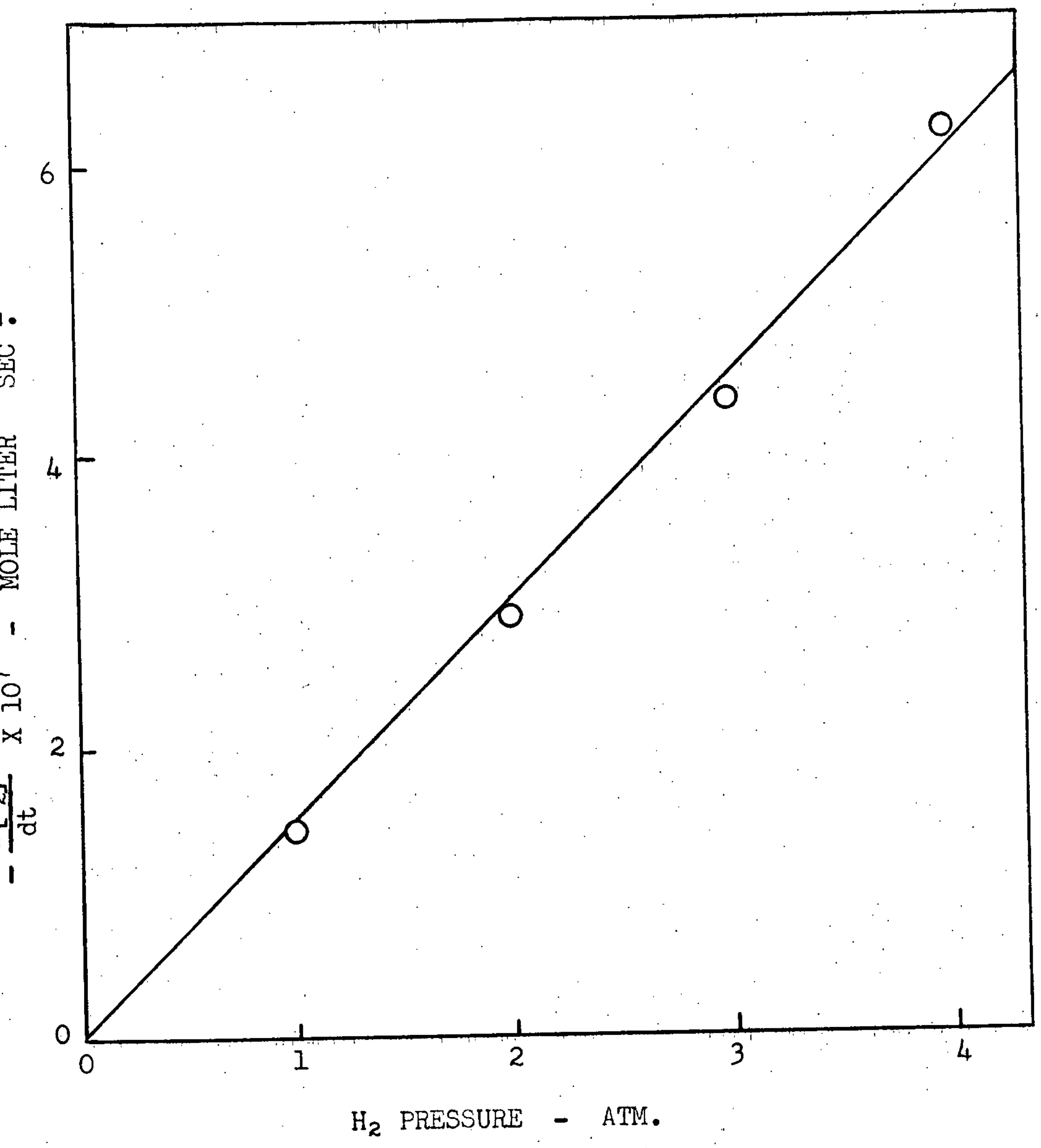


Fig. 15. Dependence of the rate on $H_2$ partial pressure at 110°C. Solutions $9.6 \times 10^{-3}$ M. $AgClO_4$; 0.03 M. $HClO_4$.

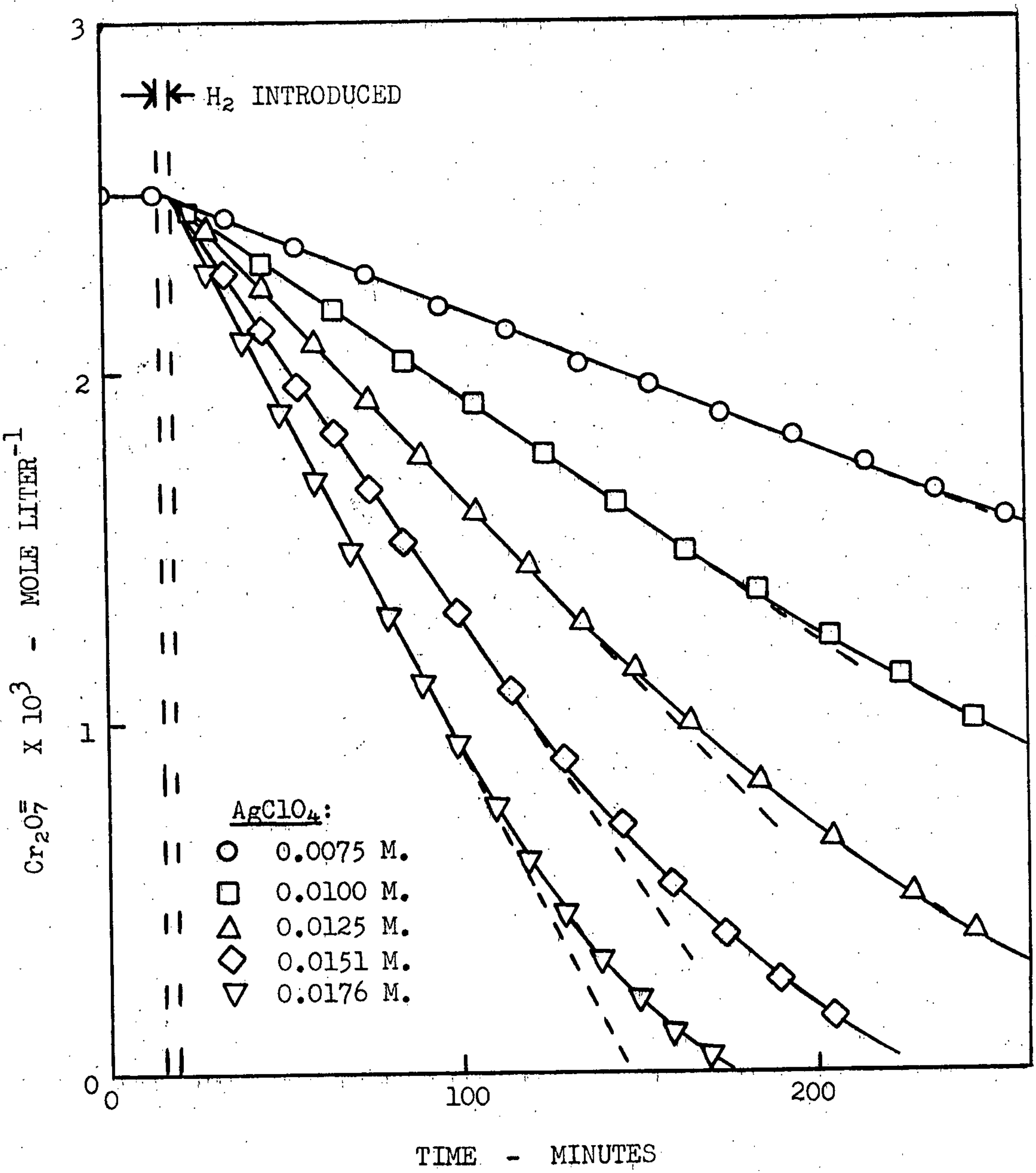


Fig. 16. Rate plots for the reaction of $Cr_2O_7^=$ with $H_2$ in solutions containing different amounts of $AgClO_4$ at 110°C. Solutions 0.1 M. $HClO_4$; $H_2$ pressure, 4.0 atm.

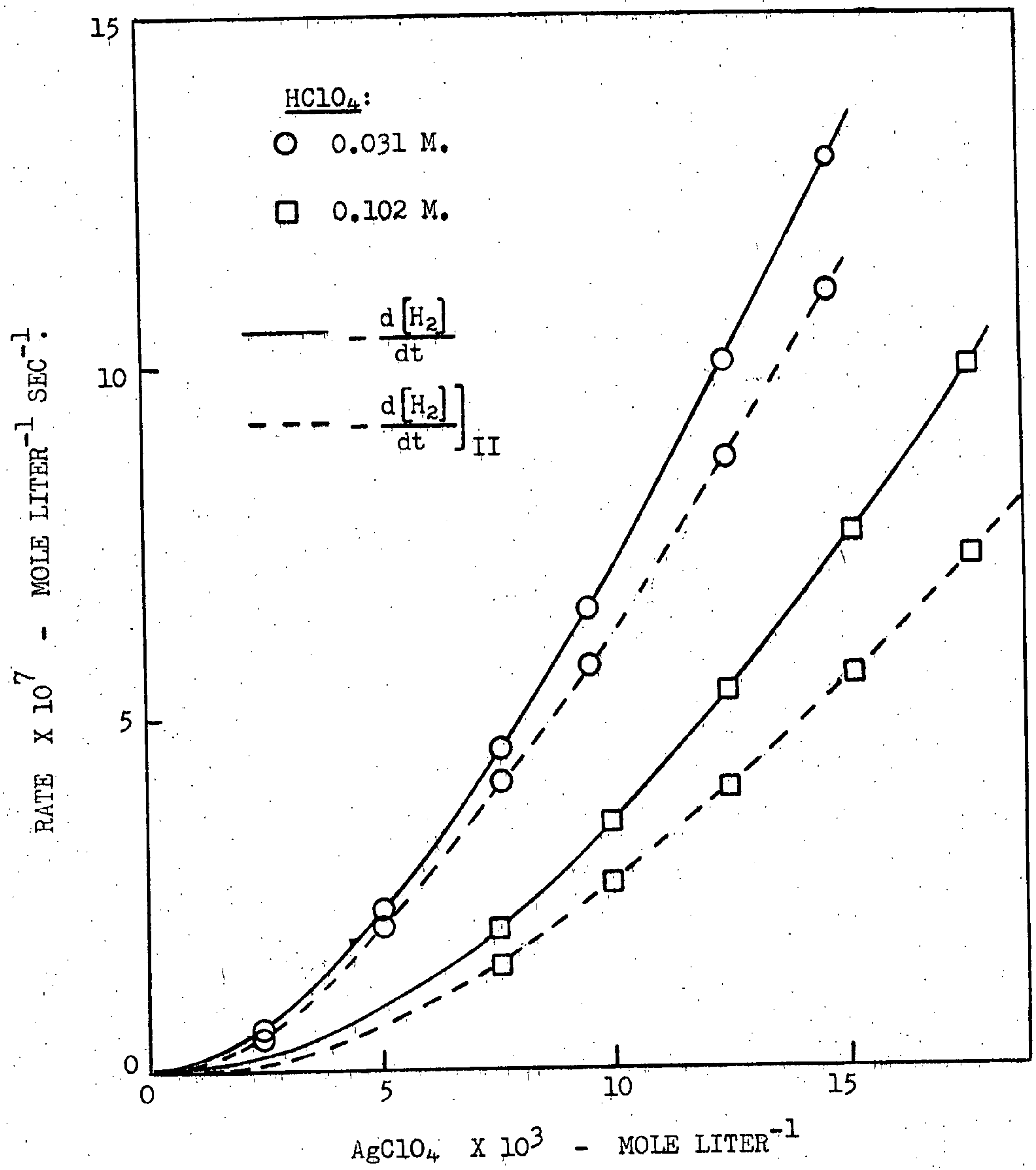


Fig. 17. Dependence of the rate on $AgClO_4$ concentration at 110°C. $H_2$ pressure, 4.0 atm.

kinetics at high temperatures. This is in marked contrast to the behaviour of the system at 50°C (see Table IV).

The results can be treated more quantitatively by application of equation (4),

$$-\left.\frac{d\,[H_2]}{dt}\right]_{II} = \frac{k_{II}[Ag^+]^2[H_2]}{k'_{II}[H^+] + [Ag^+]} \quad .$$

This equation may be rearranged to give,

$$\frac{[Ag^+]}{-\left.\frac{d[H_2]}{dt}\right]_{II}} = \frac{k'_{II}}{k_{II}[H_2]}\frac{[H^+]}{[Ag^+]} + \frac{1}{k_{II}[H_2]} \qquad \ldots\ldots (6)$$

A plot of $[AgClO_4]$/rate against $1/[AgClO_4]$ at constant acid concentration should be linear, according to equation (6). Fig. 18 shows plots of this type for both $- d[H_2]/dt$ and $- d[H_2]/dt]_{II}$; values of the latter were found with the aid of the finally determined expression for $- d[H_2]/dt]_I$. It is seen that the plots for $- d[H_2]/dt]_{II}$ are indeed linear.

Equation (6) suggests also that $1/ - d[H_2]/dt]_{II}$ should be linearly dependent upon $[HClO_4]$ at constant $Ag^+$ concentration. The results plotted in Fig. 19 (obtained at constant ionic strength) are in accord with this.

Increasing the ionic strength from 0.04 to 0.31 by the addition of sodium perchlorate (see Table VI) produced a slight decrease in the rate.

Examination of equation (6) reveals that values of $k_{II}$ and $k'_{II}$ can be calculated from the slopes and intercepts of the plots shown in Figs. 18 and 19. The results of such calculations, for various conditions, are listed in Table VII.

Reference to Table VII indicates that the values of the constants obtained by variation of the $AgClO_4$ concentrations are in reasonable agreement with each other, but that the results found by variation of the $HClO_4$ concentration are somewhat lower. This may be due in part to the

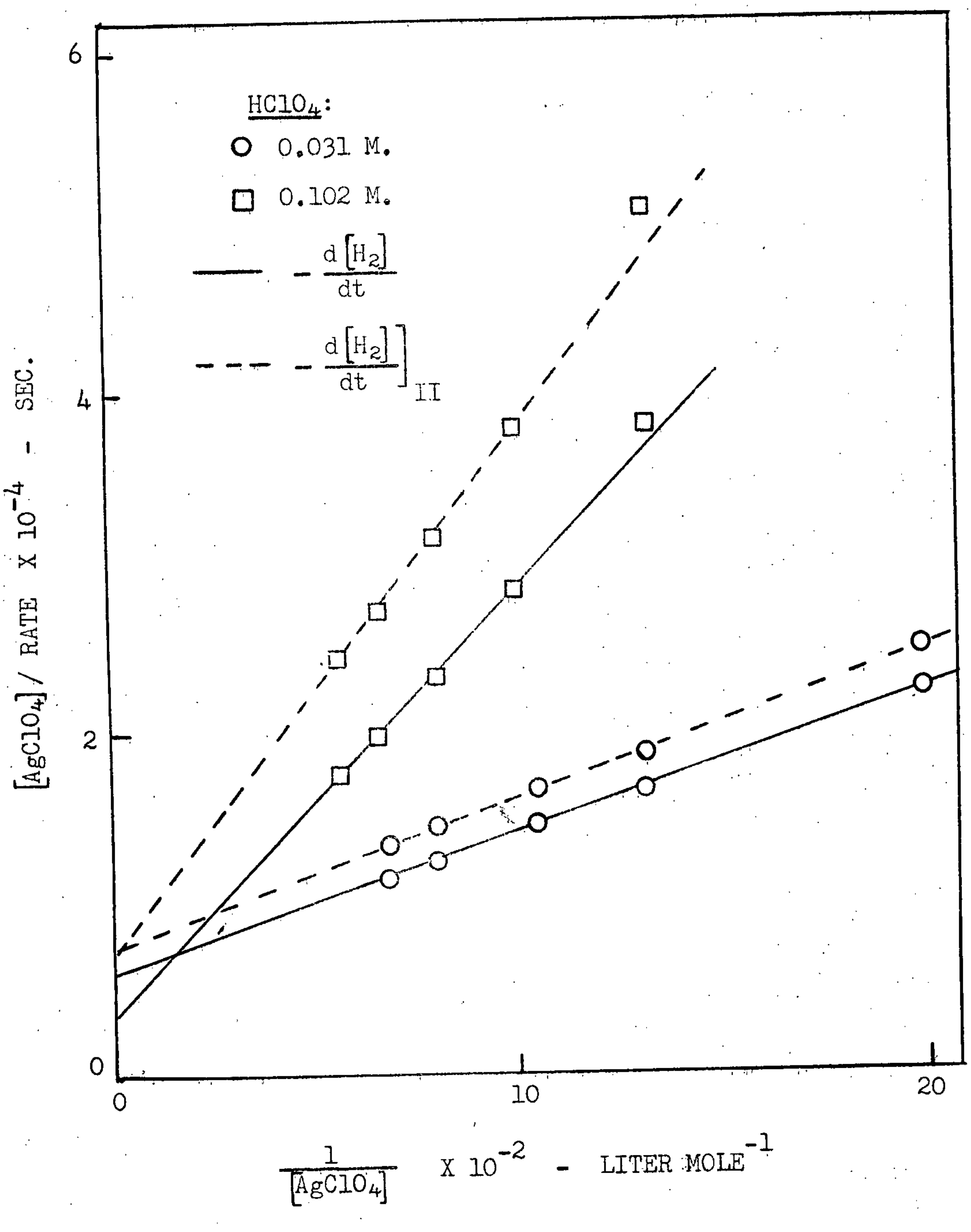


Fig. 18. Dependence of the rate on $AgClO_4$ concentration; plotted according to equation (6). Temp. 110°C; $H_2$ pressure, 4.0 atm.

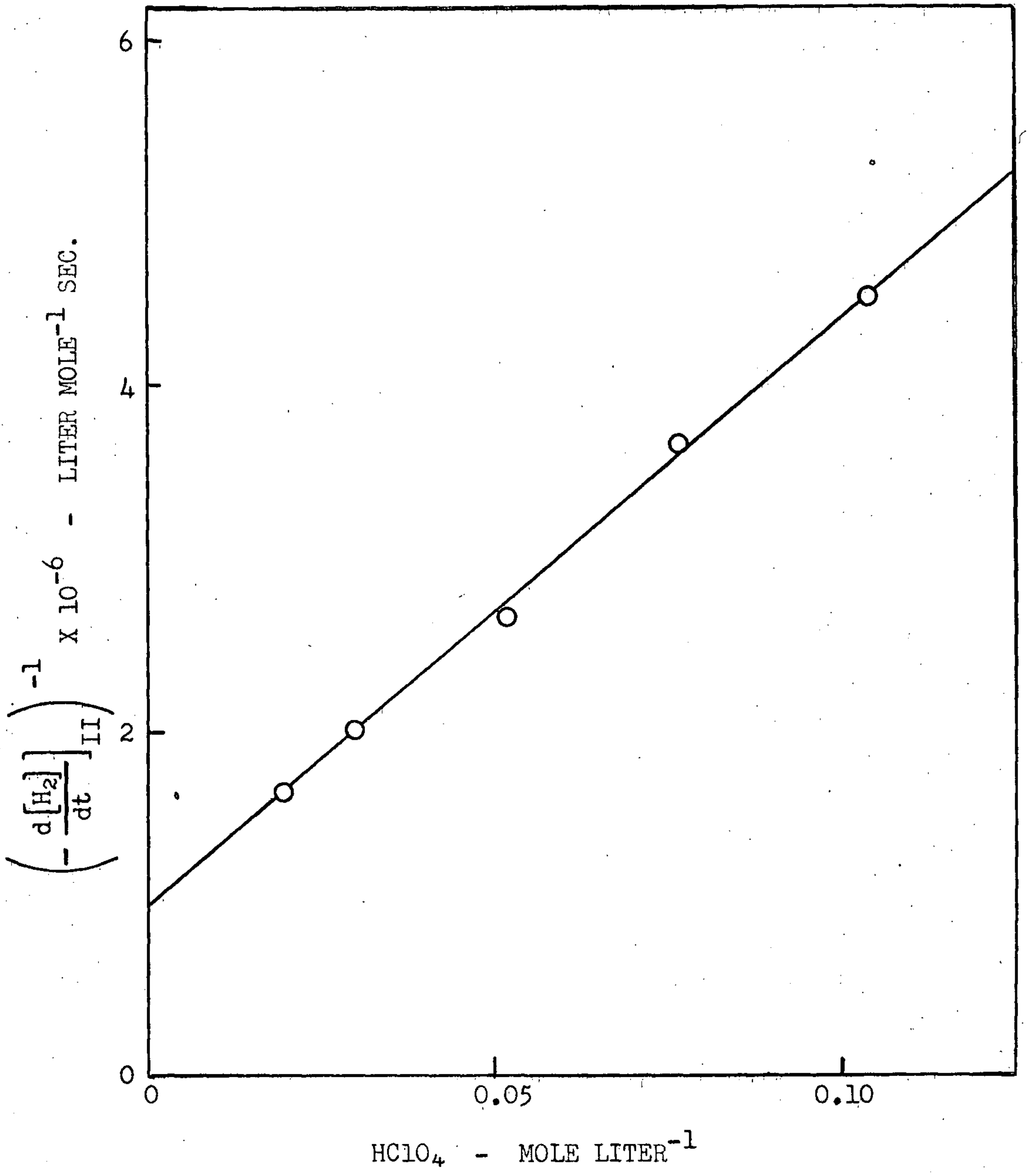


Fig. 19. Dependence of the rate on $HClO_4$ concentration; plotted according to equation (6). Temp. 110°C; solutions $9.5 \times 10^{-3}$ M. $AgClO_4$; $H_2$ pressure, 4.0 atm.

TABLE VII

Values of $k_{II}$ and $k'_{II}$ determined at temperatures from 85° to 120°C.

| Temp. °C | $k_{II}$ X $10^2$ l.mole$^{-1}$sec.$^{-1}$ | $k'_{II}$ | Determined by variation of |
|---|---|---|---|
| 110.0 | 4.1 | 0.39 | $[AgClO_4]$; with $[HClO_4]$ = 0.03 M. |
| 110.0 | 4.3 | 0.44 | $[AgClO_4]$; with $[HClO_4]$ = 0.10 M. |
| 110.0 | 3.3 | 0.33 | $[HClO_4]$; with $[AgClO_4]$ = 9.5 $10^{-3}$M. $\mu$ = 0.31 |
| 85.0 | 0.44 | 0.11 | $[AgClO_4]$; with $[HClO_4]$ = 0.03 M. |
| 100.8 | 1.8 | 0.23 | $[AgClO_4]$; with $[HClO_4]$ = 0.03 M. |
| 120.3 | 8.7 | 0.62 | $[AgClO_4]$; with $[HClO_4]$ = 0.03 M. |

higher ionic strength at which the latter experiments were carried out. It should be realized, also, that quite large errors are inherent in the method which must be used to evaluate $k_{II}$ and $k'_{II}$.

The rate plots shown in Fig. 20 were determined at temperatures from 85° to 120°C. It will be noted that the magnitude of the deviations from linearity decrease as the temperature is lowered; that is, the rate plots approach the zero order plots observed in the studies made between 30° and 70°C. By varying the $AgClO_4$ concentration, while holding the $HClO_4$ concentration constant, series of rates at different temperatures were obtained and plotted according to equation (6) (see Fig. 21). The values of $k_{II}$ and $k'_{II}$ listed in Table VII were then determined. From these data the plots of log $k_{II}$ and log $k'_{II}$ against 1/T, shown in Fig. 22, were constructed. The expressions for these constants were found to be,

$$k_{II} = 1.2 \times 10^{(12 \pm 1)} \exp[-(24 \pm 2) \times 10^3 / RT] \text{ l.mole}^{-1}\text{sec.}^{-1}$$

$$k'_{II} = 2.3 \times 10^{(7 \pm 2)} \exp[-(14 \pm 4) \times 10^3 / RT] .$$

The uncertainties in the determination of $k_{II}$ and $k'_{II}$ are intrinsically large. The values of $- d[H_2]/dt$ may be somewhat dependent upon the initial dichromate concentration, as noted previously. There are uncertainties in the magnitude of $- d[H_2]/dt]_I$ which is determined, essentially, by extrapolation from low temperature. The evaluation of $k_{II}$ involves a quite large extrapolation, while determination of $k'_{II}$ depends both upon the value of $k_{II}$ and the measurement of the slope of the plot made according to equation (6) (see Figs. 18 and 19). It is estimated that the possible errors are generally about ± 15% for $k_{II}$ and ± 25% for $k'_{II}$.

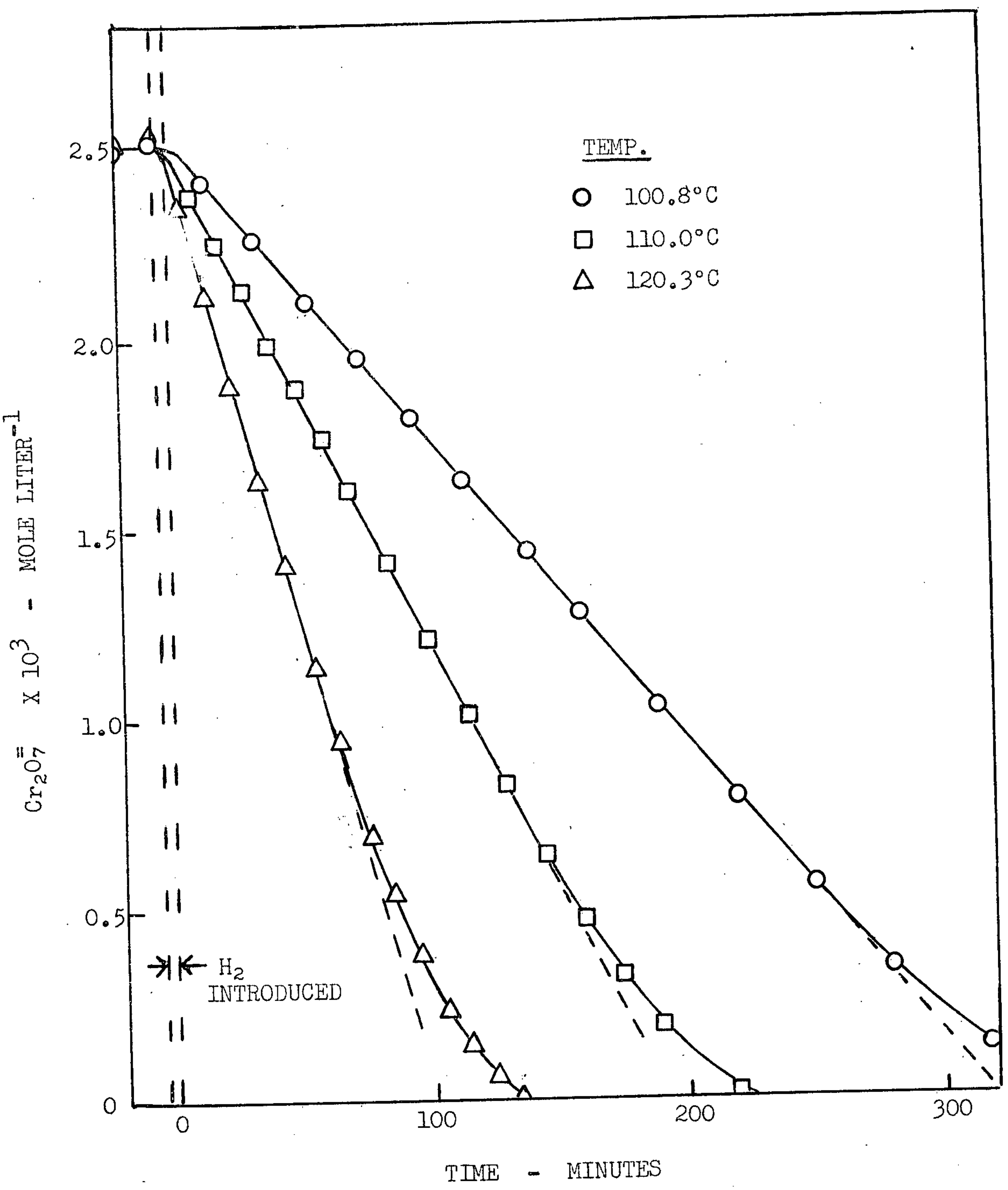


Fig. 20. Rate plots for the reduction of $Cr_2O_7^=$ by $H_2$ at different temperatures. Solutions 0.01 M. $AgClO_4$; 0.03 M. $HClO_4$.

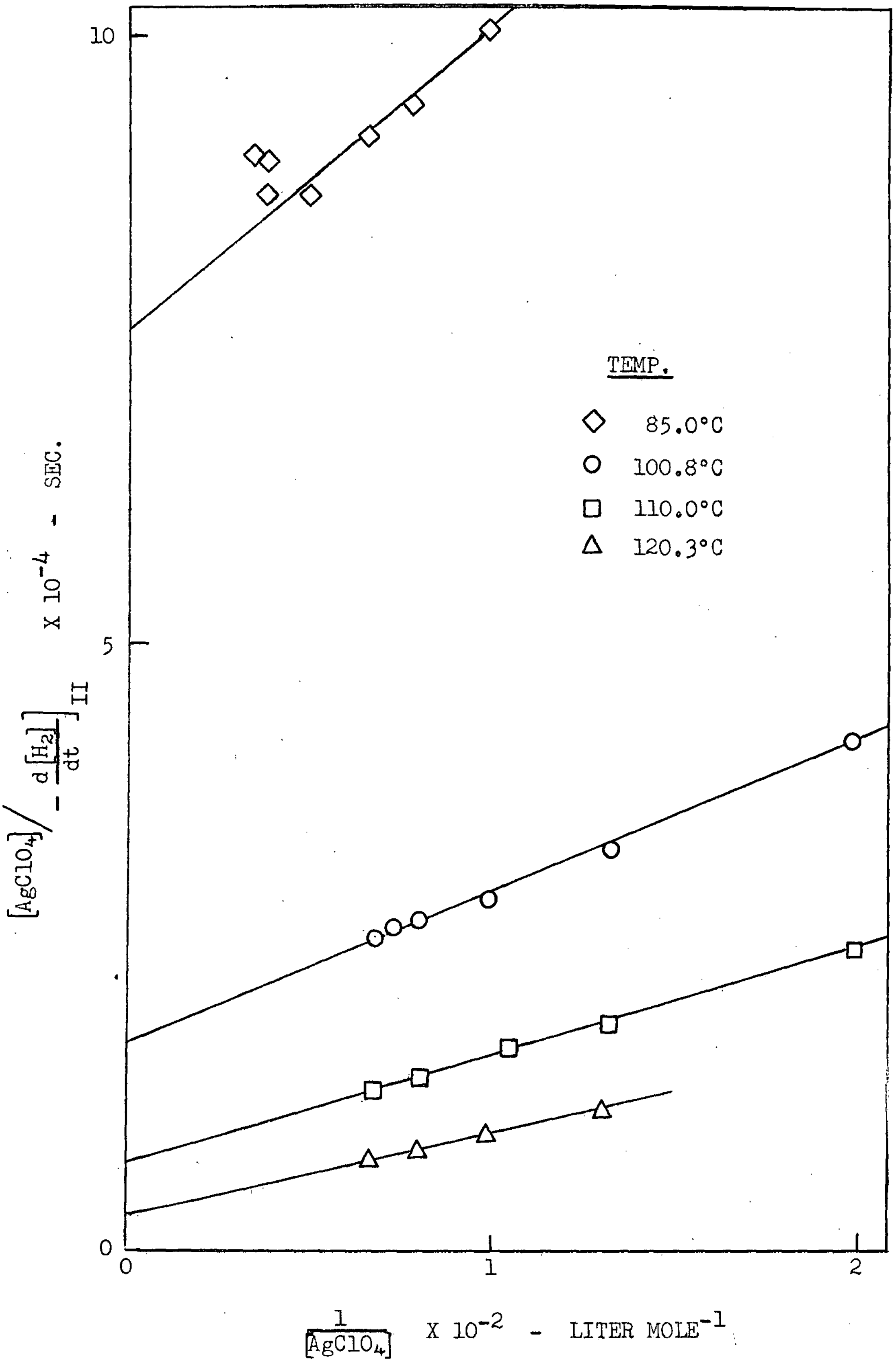


Fig. 21. Dependence of the rate on silver perchlorate concentration at different temperatures; plotted according to equation (6). Solutions 0.03 M. $HClO_4$; $H_2$ pressure, 4.0 atm.

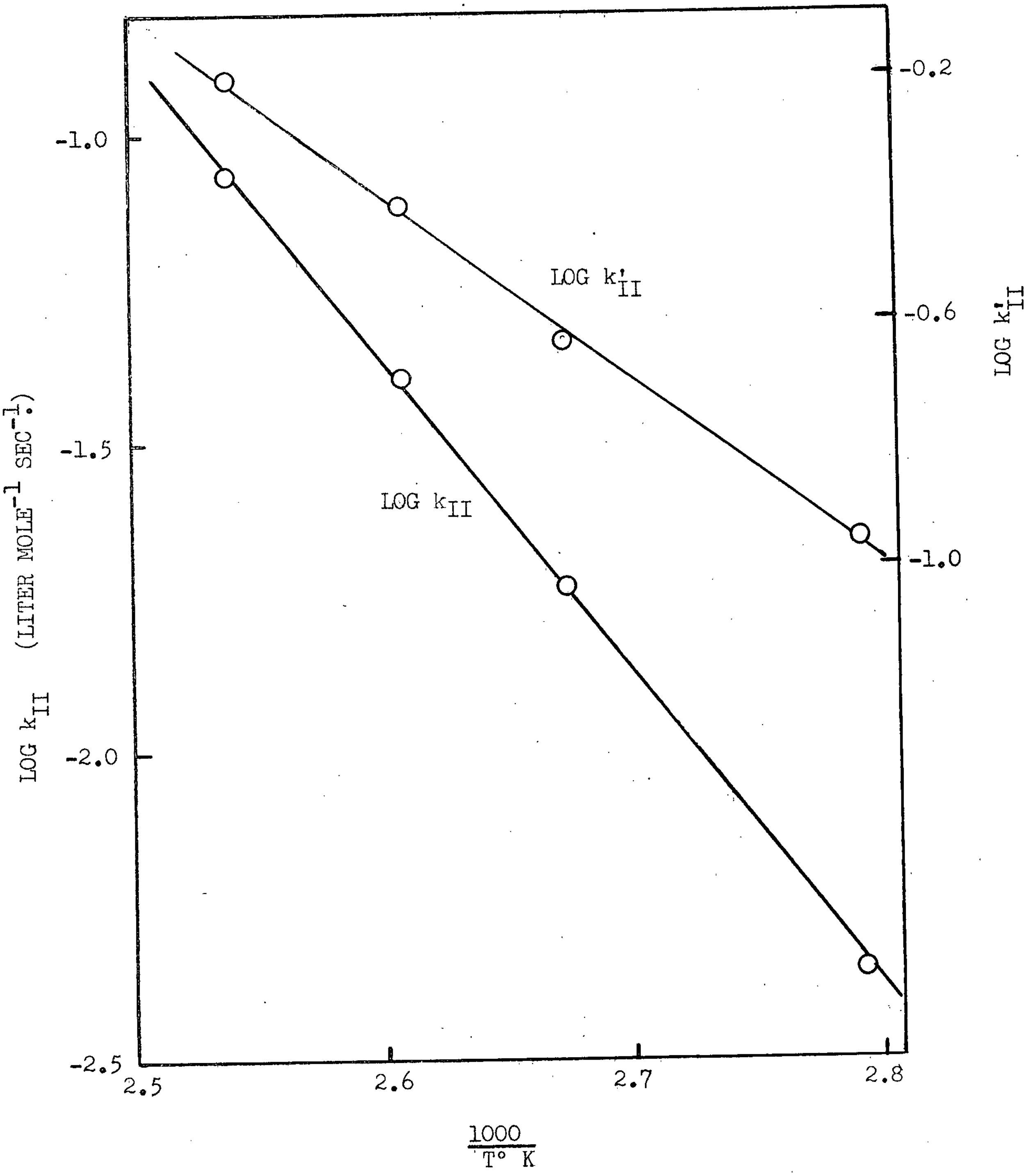


Fig. 22. Plots of LOG $k_{II}$ and LOG $k'_{II}$ against 1/T. Determinations of $k_{II}$ and $k'_{II}$ made at 0.03 M. $HClO_4$, 4.0 atm. $H_2$.

### (ii) Low dichromate concentration

From an examination of Figs. 13, 16, and 20, it may be concluded qualitatively that the deviations from linearity in the rate plots increase with (1) increasing acid concentration, (2) increasing temperature, and (3) decreasing silver ion concentration. A more detailed investigation of the rates at low dichromate concentrations was carried out using solutions with about 1.67 X $10^{-4}$ mole liter$^{-1}$ of $Cr_2O_7^=$ initially present. In Fig. 23 are found typical rate plots obtained in this investigation. These may be represented empirically by an equation of the form,

$$-\frac{d[H_2]}{dt} = (k_o + k_1 [Cr_2O_7^=]) [H_2] \qquad \ldots\ldots (7)$$

The data presented in Table VIII indicate that $k_o$ and $k_1$ are independent of the hydrogen pressure (and concentration) and of the initial $Cr_2O_7^=$ concentration, at least up to 3.35 X $10^{-4}$ M. $Cr_2O_7^=$. It is apparent that this relationship cannot hold at high dichromate concentrations since in that region the rate is independent of the concentration of the oxidizing agent. The Cr(VI) concentration is still formally represented by $Cr_2O_7^=$ in moles liter$^{-1}$, but it should be realized that this is not the only species present. It has been suggested (78) that the principal equilibrium involving Cr(VI) species under these conditions is,

$$H_2O + Cr_2O_7^= \rightleftharpoons 2\ HCrO_4^- \ .$$

Other measurements (81) indicate that the formation of $H_2CrO_4$ and $HCr_2O_7^-$ may also take place. The interpretation of the kinetic results can be simplified somewhat by considering only $k_o$, which is essentially independent of the form in which the Cr(VI) is present. Determinations of $k_o$ and $k_1$ were reproducible to about ± 5%.

Figure 24 shows rate plots for the reduction of dichromate at various

TABLE VIII

Rates of reaction between $Cr_2O_7^=$ and $H_2$ at low $Cr_2O_7^=$ concentrations

Temp. 110°C.

| Initial $Cr_2O_7^=$ X $10^4$ M. | $H_2$ Pressure atm. | $AgClO_4$ X $10^3$ M. | $HClO_4$ M. | $NaClO_4$ M. | $k_o$ X $10^5$ sec.$^{-1}$ | $k_1$ X $10^4$ l.mole$^{-1}$sec.$^{-1}$ |
|---|---|---|---|---|---|---|
| 0.98 | 4.0 | 9.55 | 0.10 | - | 0.78 | 0.97 |
| 1.67 | 4.0 | 9.57 | 0.10 | - | 0.78 | 0.97 |
| 3.35 | 4.0 | 9.59 | 0.10 | - | 0.81 | 0.95 |
| 1.67 | 1.0 | 9.44 | 0.03 | - | 2.1 | 3.0 |
| 1.67 | 2.0 | 9.48 | 0.03 | - | 2.3 | 2.8 |
| 1.67 | 3.0 | 9.56 | 0.03 | - | 2.3 | 2.8 |
| 1.67 | 4.0 | 9.54 | 0.03 | - | 2.3 | 2.7 |
| 1.67 | 4.0 | 9.55 | 0.03 | 0.03 | 2.5 | 2.6 |
| 1.67 | 4.0 | 9.58 | 0.03 | 0.07 | 2.7 | 2.3 |
| 1.67 | 4.0 | 9.52 | 0.03 | 0.17 | 2.9 | 2.1 |
| 1.67 | 4.0 | 9.56 | 0.03 | 0.27 | 3.2 | 2.0 |

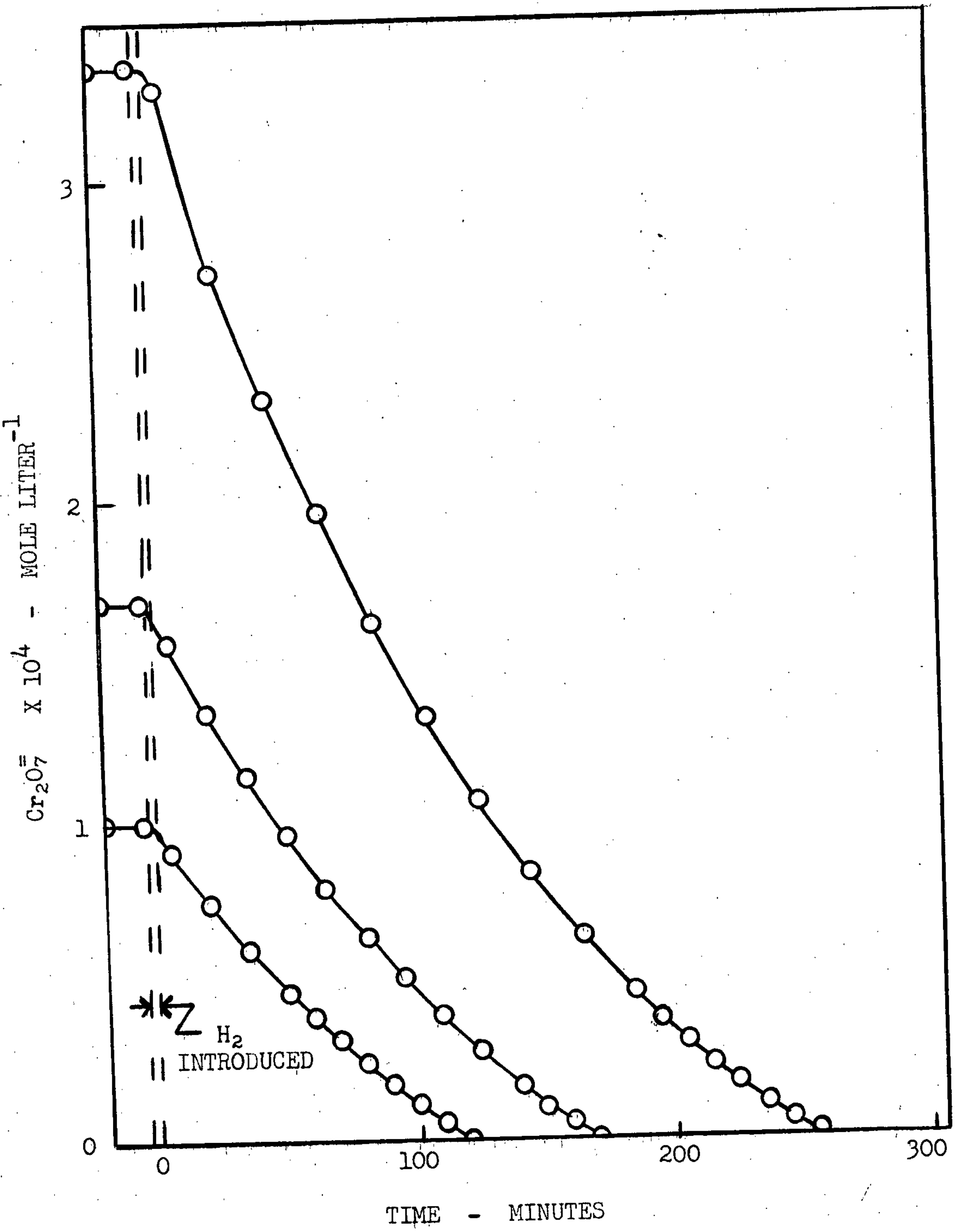


Fig. 23. Typical rate plots for the reduction of dichromate by hydrogen at low dichromate concentrations. Temp. 110°C. Solutions 9.6 X $10^{-3}$ M. $AgClO_4$; 0.10 M. $HClO_4$; $H_2$ pressure, 4.0 atm.

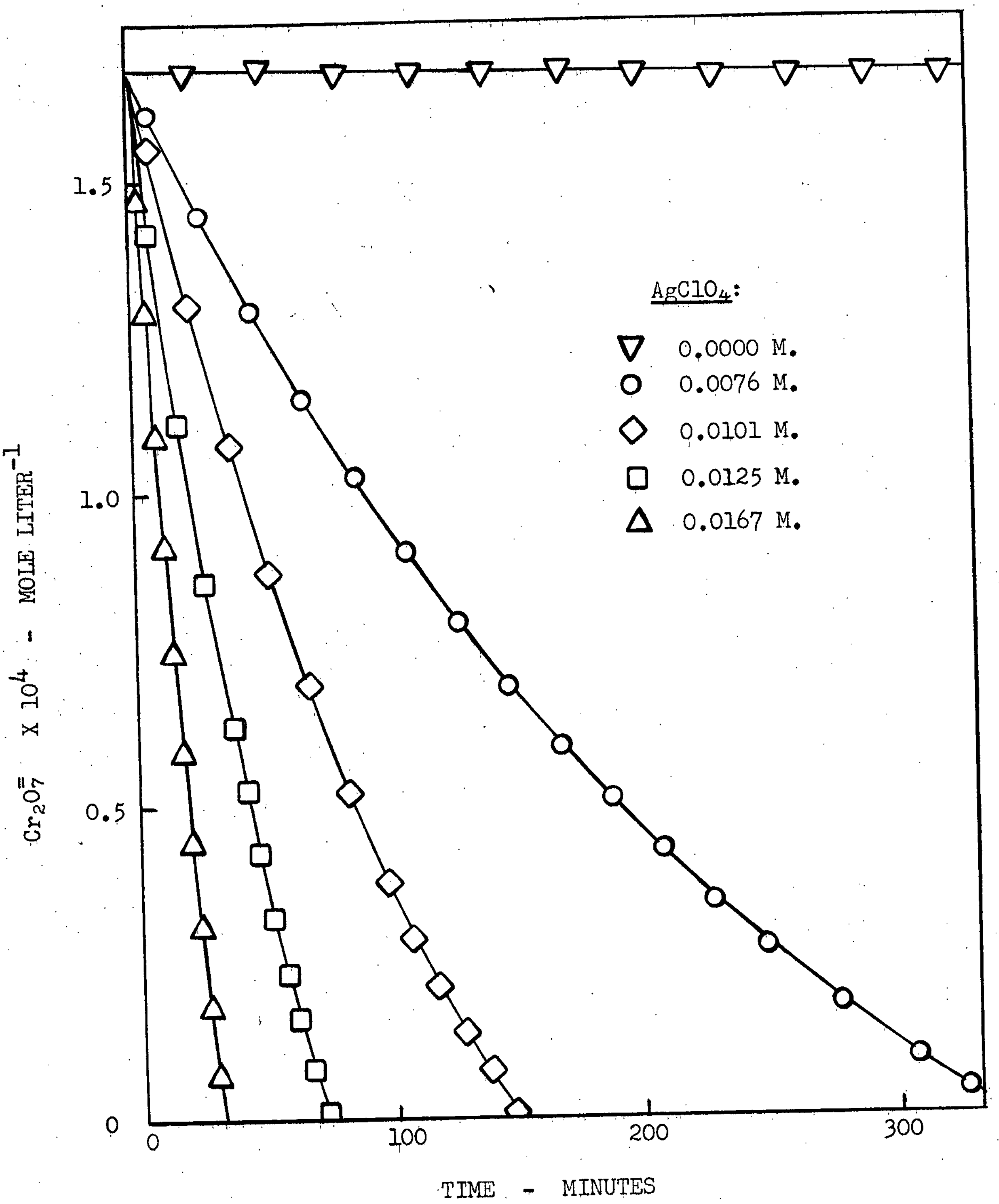


Fig. 24. Rate plots for the reduction of $Cr_2O_7^=$ by hydrogen at 110°C in solutions containing different amounts of $AgClO_4$. Solutions $1.67 \times 10^{-4}$ M. $Cr_2O_7^=$ initially; 0.1 M. $HClO_4$; $H_2$ pressure, 4.0 atm.

$AgClO_4$ concentrations; the large effect of a relatively small change in silver concentration will be noted. Values of $\kappa_0$ obtained from these plots were used to construct Fig. 25 in which a linear relation between log $\kappa_0$ and log $[AgClO_4]$ is indicated. From Fig. 25 the empirical equations,

$$\kappa_0 = 60\ [AgClO_4]^{3.4}\ \text{sec.}^{-1},\ \text{with}\ [HClO_4] = 0.1\ \text{M.}$$

and,

$$\kappa_0 = 6.8 \times 10^2\ [AgClO_4]^{3.7}\ \text{sec.}^{-1},\ \text{with}\ [HClO_4] = 0.03\ \text{M.}$$

for $\kappa_0$ were found.

The dependence of $1/\kappa_0$ on the $HClO_4$ concentration is shown in Fig. 26; from this plot the empirical equation,

$$\kappa_0 = \frac{14.4 \times 10^{-5}}{1 + 134\ [HClO_4]}\qquad \text{sec.}^{-1}$$

with $[AgClO_4] = 9.6 \times 10^{-3}$ M. may be deduced. Reference to Table VIII indicates that with increasing ionic strength $\kappa_0$ increases and $\kappa_1$ decreases. No detailed examination of the effect of temperature was made.

## Discussion

The form of equations (3), (4), and (5) appears to describe the observed kinetics adequately, when the rates are independent of the $Cr_2O_7^{=}$ concentration. Some observed rates are compared in Table IX with values of $- d[H_2]/dt$ calculated using the expressions for $k_I$, $k_{II}$, and $k'_{II}$ given earlier*. The good agreement between the observed and calculated values

---

* More explicitly, the following expressions were used,

$$\log k_I = 7.833 - \frac{14750}{4.576\ T} \qquad (\text{liter mole}^{-1}\text{sec.}^{-1})$$

$$\log k_{II} = 12.078 - \frac{23640}{4.576\ T} \qquad (\text{liter mole}^{-1}\text{sec.}^{-1})$$

$$\log k'_{II} = 7.366 - \frac{13650}{4.576\ T} \quad .$$

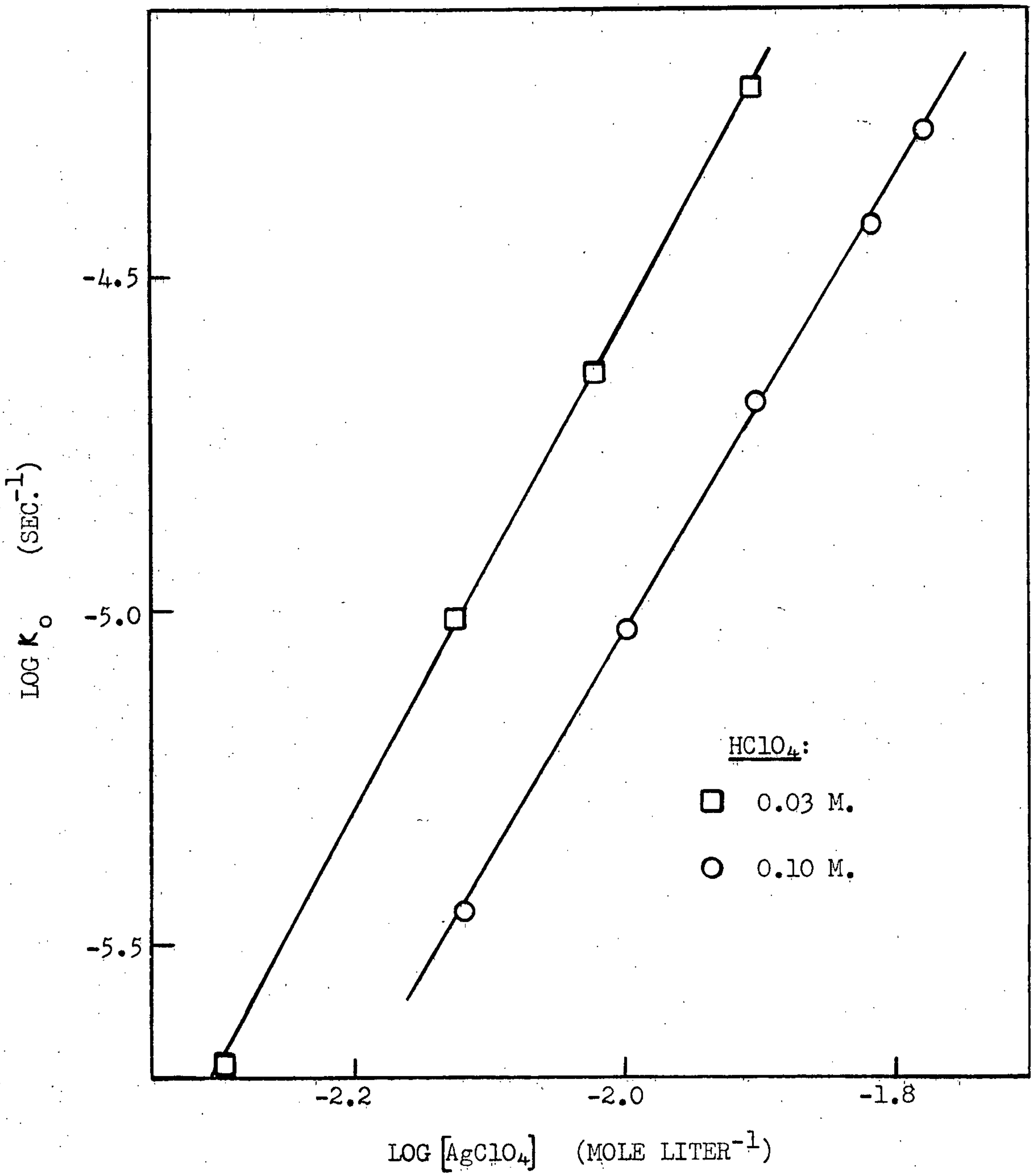


Fig. 25. Dependence of LOG $k_o$ on LOG $[AgClO_4]$. Solutions 1.67 X 10$^{-4}$ M. $Cr_2O_7^=$ initially; Temp. 110°C; determinations made at 4.0 atm. $H_2$.

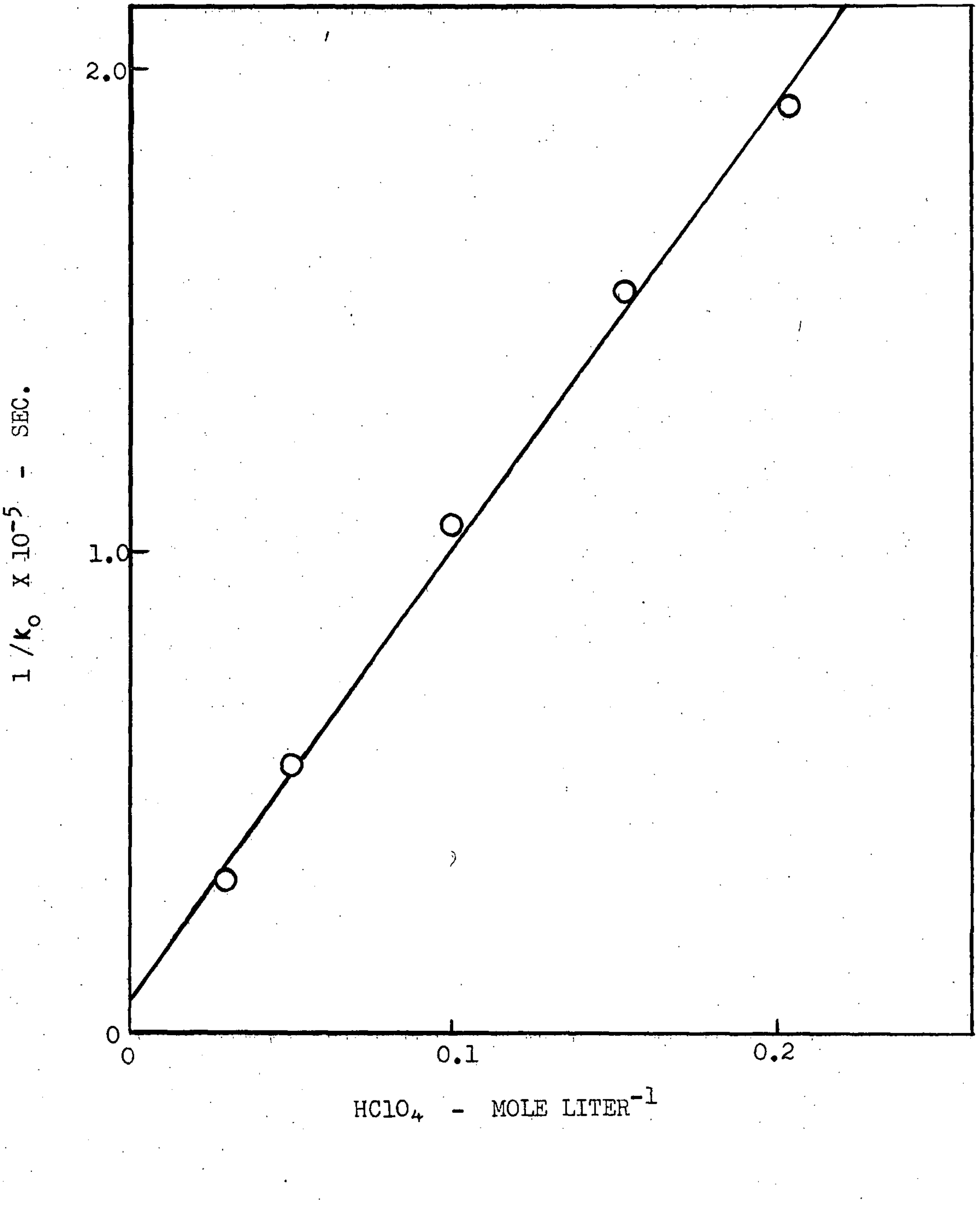


Fig. 26. Dependence of $1/k_o$ on $HClO_4$ concentration. Solutions $1.67 \times 10^{-4}$ M. $Cr_2O_7^{=}$ initially; $9.6 \times 10^{-3}$ M. $AgClO_4$; $\mu = 0.31$. Temp. 110°C; determinations made at 4.0 atm. $H_2$.

## TABLE IX

A comparison of some observed rates of reaction of hydrogen in the presence of $AgClO_4$ with the corresponding calculated rates

| Temp. | $AgClO_4$ | $HClO_4$ | $P_{H_2}$ | Calculated Rates mole liter$^{-1}$ sec.$^{-1}$ | | | Obs. Rates m.l.$^{-1}$ sec.$^{-1}$ | Discrepancy |
|---|---|---|---|---|---|---|---|---|
| °C | M. | M. | atm. | $\left.\frac{-d[H_2]}{dt}\right]_I$ X $10^8$ | $\left.\frac{-d[H_2]}{dt}\right]_{II}$ X $10^8$ | $\frac{-d[H_2]}{dt}$ X $10^8$ | $\frac{-d[H_2]}{dt}$ X $10^8$ | |
| 30 | 0.100 | 0.5 | 0.948 | 1.16 | 0.08 | 1.24 | 1.22 | +2% |
| 50 | 0.0395 | 0.5 | 0.878 | 0.72 | 0.27 | 0.99 | 1.03 | -4% |
| 70 | 0.0402 | 0.5 | 0.705 | 2.28 | 1.37 | 3.65 | 3.64 | - |
| 70 | 0.1001 | 0.5 | 0.693 | 13.9 | 4.3 | 18.2 | 17.7 | +3% |
| 85 | 0.0151 | 0.0310 | 4.0 | 4.65 | 16.6 | 21.3 | 21.0 | +1% |
| 85 | 0.0279 | 0.0324 | 4.0 | 15.8 | 33.4 | 49.2 | 46.8 | +5% |
| 110 | 0.00995 | 0.1014 | 4.0 | 8.76 | 26.9 | 35.7 | 35.0 | +2% |
| 110 | 0.01249 | 0.0309 | 4.0 | 13.8 | 85.1 | 98.9 | 100.2 | -1% |

over a wide range of conditions may be seen from the selection of the results presented. It will be noted that this agreement holds for rates which are composed of contributions of comparable magnitude from both $-d[H_2]/dt]_I$ and $-d[H_2]/dt]_{II}$. The possibility exists, of course, that some other rate law might be constructed which would fit the observations, but it is unlikely that it would have as simple a form as the rate law considered here.

The formulation of the rate equation as the sum of two terms implies the existence of two parallel mechanisms. It will be convenient to consider the mechanisms in a slightly different order from the sequence in which the results were presented. First, the mechanism (II), corresponding to $-d[H_2]/dt]_{II}$, will be discussed, followed by an interpretation of the results at low $Cr_2O_7^=$ concentration; finally the mechanism (I) will be considered.

(i) Mechanism of path (II)

The form of the rate expression,

$$-\left.\frac{d[H_2]}{dt}\right]_{II} = \frac{k_{II}[Ag^+]^2[H_2]}{k'_{II}[H^+] + [Ag^+]}$$

suggests a mechanism similar to that proposed for the $Cu^{++} - H_2$ reaction in perchloric acid (55). The first step in such a scheme is the formation of an intermediate hydride with the release of a proton,

$$Ag^+_{aq} + H_2 \xrightarrow{k_1} AgH_{aq} + H^+_{aq} \qquad \text{...... (8)}$$

Silver ion then competes with hydrogen ion for this intermediate,

$$H^+ + AgH \xrightarrow{k_{-1}} Ag^+ + H_2 \qquad \text{...... (8a)}$$

$$Ag^+ + AgH \xrightarrow{k_2} \text{intermediates} \xrightarrow{\text{fast}} \text{products} \qquad \text{.. (9)}$$

In the presence of the $Cr_2O_7^=$, the intermediates in equation (9) reduce

Cr(VI) to Cr(III) with the regeneration of silver ions. Since the postulated intermediate AgH will be unstable, it will not be present in macroscopic concentration; the steady state condition, $-d[AgH]/dt = 0$, may therefore be applied. The rate equation,

$$-\left.\frac{d[H_2]}{dt}\right]_{II} = \frac{k_1[Ag^+]^2[H_2]}{(k_{-1}/k_2)[H^+] + [Ag^+]} \quad \ldots\ldots (10)$$

then follows, in which identification is made between $k_1$ and $k_{II}$, and between the ratio $k_{-1}/k_2$ and $k'_{II}$.

From the known expression for $k_{II}$ it follows that the step represented by equation (8) takes place with $\Delta H^{\ddagger} = 23 \pm 2$ kcal. mole$^{-1}$ and $\Delta S^{\ddagger} = -6 \pm 5$ cal. deg.$^{-1}$mole$^{-1}$ at 110°C (standard states are hypothetical 1 mole liter$^{-1}$). This entropy of activation appears to be, within experimental error, normal for a second order reaction (82).

This interpretation requires that the endothermicity of reaction (8) should not be greater than the activation energy assigned to this step, i.e. $23 \pm 2$ kcal. mole$^{-1}$. The endothermicity of the reaction,

$$Ag^+_{aq} + H_{2\,g} \longrightarrow AgH_g + H^+_{aq}$$

may be estimated as 42 kcal. mole$^{-1}$ from thermochemical data (83). The principal uncertainty in this calculation is in the heat of formation of $AgH_g$, estimated to be $\pm$ 6 kcal. mole$^{-1}$ (84). The heat of solvation of the "silver hydride" may be reasonably large, since it is possible that the molecule is quite polar, $\overset{\delta+}{Ag}\overset{\delta-}{H}$; the endothermicity of the reaction forming $AgH_{aq}$ would then be much lower than the 42 kcal. quoted above, i.e. consistent with an activation energy of $23 \pm 2$ kcal. mole$^{-1}$. In this connection it should be noted that the intermediate AgH has also been proposed in a mechanism for the reduction of AgOAc in pyridine (39).

Other schemes for the first reaction step between $Ag^+$ and $H_2$ correspond to even higher endothermicities, and are therefore even more difficult to reconcile with the experimental results, for example,

$$Ag^+_{aq} + H_{2\,g} \longrightarrow Ag^o_g + H_g + H^+_{aq} \qquad \Delta H = +95 \text{ kcal.}$$

It is unlikely that the solvation energies of the atomic species $Ag^o$ and H are very large. A reaction of the type,

$$Ag^+_g + H_2 \longrightarrow Ag^o_g + H_2{}^+_g \qquad \Delta H = +179 \text{ kcal.}$$

would be unlikely since the difference between the solvation energies of $Ag^+$ and $H_2{}^+$ would probably be too small to lower the endothermicity to the point where it would be consistent with the observed activation energy.

In the proposed mechanism (reactions (8), (8a), and (9) ) the ratio $k_{-1}/k_2$ is the quotient of two bimolecular rate constants, which might be expected to have frequency factors of comparable magnitude. However, the experimental values of $k'_{II}$ lead to a value of the ratio $A_{-1}/A_2$ of the order of 2 X $10^7$, which corresponds to a difference of activation entropies $\Delta S^{\ddagger}_{-1} - \Delta S^{\ddagger}_2 = 34 \pm 10$ cal. deg.$^{-1}$mole$^{-1}$. The difference between the apparent enthalpies of activation is correspondingly high, $\Delta H^{\ddagger}_{-1} - \Delta H_2{}^{\ddagger} = 14 \pm 4$ kcal. mole$^{-1}$. A possible explanation of the large apparent difference in frequency factors is that the formation of the activated complex from AgH and $H^+$ is accompanied by an abnormal entropy increase resulting from "desolvation of the proton", while the reverse effect (i.e. an abnormal entropy decrease resulting from "incipient proton hydration" in the activated complex) may accompany the competing reaction between AgH and $Ag^+$. A pre-equilibrium in this reaction of the type,

$$AgH + Ag^+ \overset{K}{\rightleftharpoons} Ag_2H^+ \qquad \text{(exothermic)}$$

followed by,

$$Ag_2H^+ \xrightarrow{k'_2} \text{intermediates} \xrightarrow{\text{fast}} \text{products.}$$

where $k_2 = K\,k'_2$, might be possible. If the formation of $Ag_2H^+$ were exothermic and the activation energy of $k_2'$ were small, $k_2$ could have a negative temperature coefficient. Here again a low entropy of activation would have to be assumed. It is impossible, however, to verify in detail any schemes of this type. The determination of the temperature dependence of the ratio $k_{-1}/k_2$ for the $Cu^{++}$ catalysed reduction of dichromate would be of interest.

(ii) Low dichromate concentration

In the region of low dichromate concentration at 110°C, the mechanism can only be discussed qualitatively. The complexity of the reaction, exemplified by the high order dependence upon $AgClO_4$ concentration, and the uncertainty in the exact form of the Cr(VI), preclude any detailed treatment. It would appear, however, that the following points should be considered in a treatment of the variation of $\kappa_0$.

(1) There appears to be a back reaction competing with $Cr_2O_7^=$ for the reaction intermediates.

(2) The marked decrease in $\kappa_0$ with increasing $HClO_4$ indicates that the back reaction involves $H^+$.

(3) The high order dependence of $\kappa_0$ on $AgClO_4$ concentration indicates the aggregation of a number of $Ag^+$ ions into an intermediate. Such an aggregation is to be expected for a process involving incipient nucleation (85).

(4) The aggregation process is not of the type, intermediate plus intermediate, since the rate is directly proportional to the partial pressure of hydrogen.

These general points may be summarized by a formal scheme,

$$n\,Ag^+ + H_2 \underset{steps}{\overset{intermediate}{\rightleftharpoons}} [Ag_nH]^{(n-1)+} + H^+$$

$$[Ag_nH^+]^{n-1} + Ag^+ \longrightarrow [Ag_{n+1}H]^{n+} \xrightarrow{fast} \text{reaction products}$$

The mean value of "n" attained in the aggregation process will depend on the concentrations of Cr(VI) and acid.

Reference to Table X will show that the observed values of $\kappa_o[H_2]$ (i.e. the final rates as Cr(VI) → 0) may be less than the calculated values of $-d[H_2]/dt]_I$. This would indicate that the reaction (I) is also reversible under conditions of low Cr(VI) concentration and high temperature.

(iii) Mechanism of path (I)

The kinetics of the reaction path (I),

$$-\left.\frac{d[H_2]}{dt}\right]_I = k_I[Ag^+]^2[H_2]$$

indicate a termolecular process involving two $Ag^+$ ions and one $H_2$ molecule. The intermediate produced by this combination would then react rapidly with $Cr_2O_7^=$ to yield the observed products. The entropy of activation, -25 ± 2 cal. deg.$^{-1}$mole$^{-1}$ would appear reasonable for a termolecular process.

An alternative to a termolecular step would be a scheme such as,

$$2\,Ag^+ \rightleftharpoons Ag_2^{++} \quad \text{(fast)}$$

$$Ag_2^{++} + H_2 \longrightarrow \text{intermediates} \longrightarrow \text{products}$$

This would not be kinetically distinguishable from the termolecular process unless the dimer $Ag_2^{++}$ were present in quite high concentration. Evidence from the Raman spectra of solutions of silver salts indicates that no dimer is present in concentrations greater than 0.1% of the total silver (86).

## TABLE X

A comparison of observed values of $\kappa_o[H_2]$ and calculated values of $-d[H_2]/dt]_I$ at 110°C, 4.0 atm. $H_2$

| $AgClO_4 \times 10^2$ M. | $HClO_4$ M. | $\kappa_o[H_2] \times 10^8$ mole l.$^{-1}$sec.$^{-1}$ | $-d[H_2]/dt]_I \times 10^8$ mole l.$^{-1}$sec.$^{-1}$ |
|---|---|---|---|
| 0.763 | 0.1 | 1.2 | 5.1 |
| 1.67 | 0.1 | 17.4 | 24.4 |
| 0.506 | 0.03 | 0.69 | 2.2 |
| 1.25 | 0.03 | 20.3 | 13.6 |

This mechanism is not intrinsically any more probable than a termolecular step (87). A pre-equilibrium involving $AgH_2^+$ would appear unlikely, since this species would be expected to form $AgH + H^+$.

The product of the rate controlling step cannot be known precisely, but might possibly be approximated by one of the schemes,

(1) $Ag_2H_2^{++}$ (2) $Ag_2H^+ + H^+$ (3) $2\ (AgH^+)$
(4) $2\ Ag^o + 2\ H^+$ or (5) $Ag_2 + 2\ H^+$ .

Formulations involving H atoms have been neglected since these probably would be energetically unfavourable. The intermediate (1) would probably be unstable with respect to (2) on account of the high energy of solvation of the proton. The species in (4) and (5) are improbable on energetic grounds; the reactions producing $2\ Ag^o$ and $Ag_2$ with $2\ H^+$ ions are endothermic by 88 and 47 kcal. $mole^{-1}$, respectively*, neglecting solvation of the $Ag^o$ or $Ag_2$. By analogy with the species $CuH^+$, which is believed to be the intermediate in the activation of $H_2$ by $Cu^{++}$ and $Cu^+$, representation (3), i.e. $AgH^+$ appears to be a reasonable possibility. Energetically, $2\ AgH^+$ would probably be favoured over $Ag_2H^+$ since the Ag - H bond (84) is stronger than the Ag - Ag bond (88) by about 16 kcal.

The essential independence of the rate, within fairly wide limits, of $H^+$ and $ClO_4^-$ concentrations provides some support for the conclusion that the observed activity is associated with $Ag^+$ ions rather than with $OH^-$ or $ClO_4^-$ complexes, whose concentrations in these solutions is probably small. The apparent absence of a salt effect is inconclusive since the measurements refer to a concentration region in which the Debye - Hückel theory does not apply. The commonly noted tendency for the activity coefficients of many electrolytes (89), particularly salts of polyvalent cations (which the activated complex would approximate) to increase at very high ionic strength may account for the observed slight decrease in rate when the $NaClO_4$ concentration was increased above 1 M. A salting out of $H_2$ under these conditions might also contribute to a decreased rate.

---

* Calculated on the basis of thermochemical data (83) and the spectroscopic dissociation energy of $Ag_2$ (88).

## B. EXCHANGE EXPERIMENTS

An examination of the mechanism proposed for the activation of hydrogen by silver ions given in equations (8), (8a), and (9) will indicate that the presence of deuterium oxide in the aqueous solvent should give rise to HD according to the reaction,

$$D^+ + AgH \xrightarrow{k_{-1}^{D}} Ag^+ + HD \qquad \ldots\ldots (11)$$

The HD produced would accumulate in the gas phase above the solution.

A set of four experiments was carried out to investigate this exchange. The results of these experiments were interpreted on the basis of the following assumptions.

(1) The total acid ($HClO_4$) added = $[H^+] + [D^+]$, where $[H^+]$ and $[D^+]$ are the effective concentrations of "acidic" hydrogen and deuterium.

(2) There is no isotope effect, i.e. $k_{-1}^{H} = k_{-1}^{D}$. This assumption is not justified ā priori, but is made to facilitate calculation in the absence of information on the magnitude of the ratio $k_{-1}^{H}/k_{-1}^{D}$. This point will be reconsidered in the discussion of the results.

(3) Reactions such as,

$$HD + Ag^+ \longrightarrow AgH + D^+$$

$$\text{or} \quad HD + Ag^+ \longrightarrow AgD + H^+$$

may be neglected because of the low HD content of the gas.

The following notation will be employed,

$r_o$ = rate of reaction, $-\,d[H_2]/dt$, mole $l.^{-1}sec.^{-1}$ (at 1 atm. $H_2$ pressure) extrapolated to $[H^+] = 0$ on the basis of results of Section A.

$r$ = rate of reaction, $-\,d[H_2]/dt$, mole $l.^{-1}sec.^{-1}$ (at 1 atm. $H_2$ pressure) for the $H^+$ and $Ag^+$ ion concentrations under consideration, as determined from results of Section A.

$v$ = volume of reacting solution in liters.

$V$ = volume of gas in liters.

$n$ = $\frac{[D^+]}{[H^+] + [D^+]}$, the fraction of the "acid" which is present as deuterium.

$N$ = number of moles of HD in the gas phase.

$x$ = mole fraction of HD in the gas phase.

Other symbols have their usual meaning.

The rate of formation of HD will depend on the rate of the back reaction, $(r_o - r)$; hence,

$$\frac{dN}{dt} = (r_o - r)\,Pvn.$$

Since, $$N = x\,\frac{PV}{RT},$$

then, $$dx = (r_o - r)\,\frac{v\,n\,R\,T}{V}\,dt \qquad \ldots\ldots (12)$$

From this relationship the expected HD content of the gas, x, may be estimated for any time, as illustrated in Appendix B. The values of "n" were determined on the basis of the known deuterium content of the solution and the following thermodynamic data:

(i) $E^o$ for $D_2 | D^+ = -3.4$ mv. (90), from which $K_1 = \frac{P_{D_2} [H^+]^2}{P_{H_2} [D^+]^2} = 1.31$

(ii) $D_{2\,g} + H_2O_{\,l} \rightleftharpoons H_{2\,g} + D_2O_{\,l}$

$$K_2 = \frac{P_{H_2} [D_2O]}{P_{D_2} [H_2O]} = 13.51$$

assuming $H_2O$ and $D_2O$ form ideal solutions (77).

(iii) $D_2O_{\,l} + H_2O_{\,l} \rightleftharpoons 2\ HDO_{\,l}$

$$K_3 = 3.78$$

assuming the vapour pressure of HDO to be the geometric mean of the vapour pressures of $H_2O$ and $D_2O$ (77).

The calculated values of "n" were found for 20°C, and in the absence of data for the temperature dependence of $E^o_{D_2,D^+}$ these figures were used for 110°C. The true values of "n" will probably be larger than those used here.

A comparison of the observed and calculated HD contents of the hydrogen gas is given in Table XI. The observed data is plotted in Fig. 27 together with the rate curves for the reduction of dichromate. It will be seen that the results of the exchange experiments lend some support to the mechanism postulated for the activation of $H_2$ by silver ion. Although exact quantitative agreement was not obtained, similar trends are shown by the observed and calculated exchange rates. The absence of exchange in the absence of $AgClO_4$ indicates that the effect is due to the presence of silver ion. The rate of the exchange, for a given $AgClO_4$ concentration, increases with increasing acid concentration. This observation is consistent with a back reaction involving hydrogen ion.

## TABLE XI

(a) Exchange Experiments - HD content of the gas phase

| Expr. | Time<br>min. | $x \times 10^2$<br>calc. ± 15% | <br>obs. ± 0.02 | | calc. x / obs. x |
|---|---|---|---|---|---|
| A | 35 | 0 | 0.03 | | - |
| | 155 | 0 | 0.01 | | - |
| B | 35 | 0.10 | 0.05 | | 2.0 ± 0.8 |
| | 85 | 0.25 | 0.10 | | 2.5 ± 0.6 |
| | 145 | 0.43 | 0.20 | | 2.2 ± 0.5 |
| C | 45 | 0.18 | 0.05 | | 2.8 ± 0.8 |
| | 90 | 0.36 | 0.18 | | 2.0 ± 0.8 |
| | 140 | 0.56 | 0.32 | | 1.8 ± 0.3 |
| D | 60 | 0.18 | $0.07_5$ | | 2.4 ± 1 |
| | 120 | 0.36 | 0.24 | | 1.5 ± 0.5 |
| | 180 | 0.54 | 0.32 | | 1.7 ± 0.3 |
| | | | | Mean | 2.1 ± 0.6 |

(b) Exchange Experiments - Rates of reaction

| Expr. | $AgClO_4$<br>M. | $HClO_4$<br>M. | $\frac{D}{H + D}$<br>mole fr. | $r \times 10^7$ in $H_2O - D_2O$<br>m. $l.^{-1}$ $sec.^{-1}$ $atm.^{-1}$ | $r \times 10^7$ in $H_2O$<br>m. $l.^{-1}$ $sec.^{-1}$ $atm.^{-1}$ |
|---|---|---|---|---|---|
| A | 0 | 0.1 | 0.242 | - | - |
| B | 0.010 | 0.03 | 0.198 | 1.74 | 1.77 |
| C | 0.010 | 0.10 | 0.180 | 1.09 | 0.86 |
| D | 0.0075 | 0.10 | 0.175 | 0.48 | 0.49 |
| E | 0.010 | 0.10 | 0.198 | 0.87 | 0.85 |

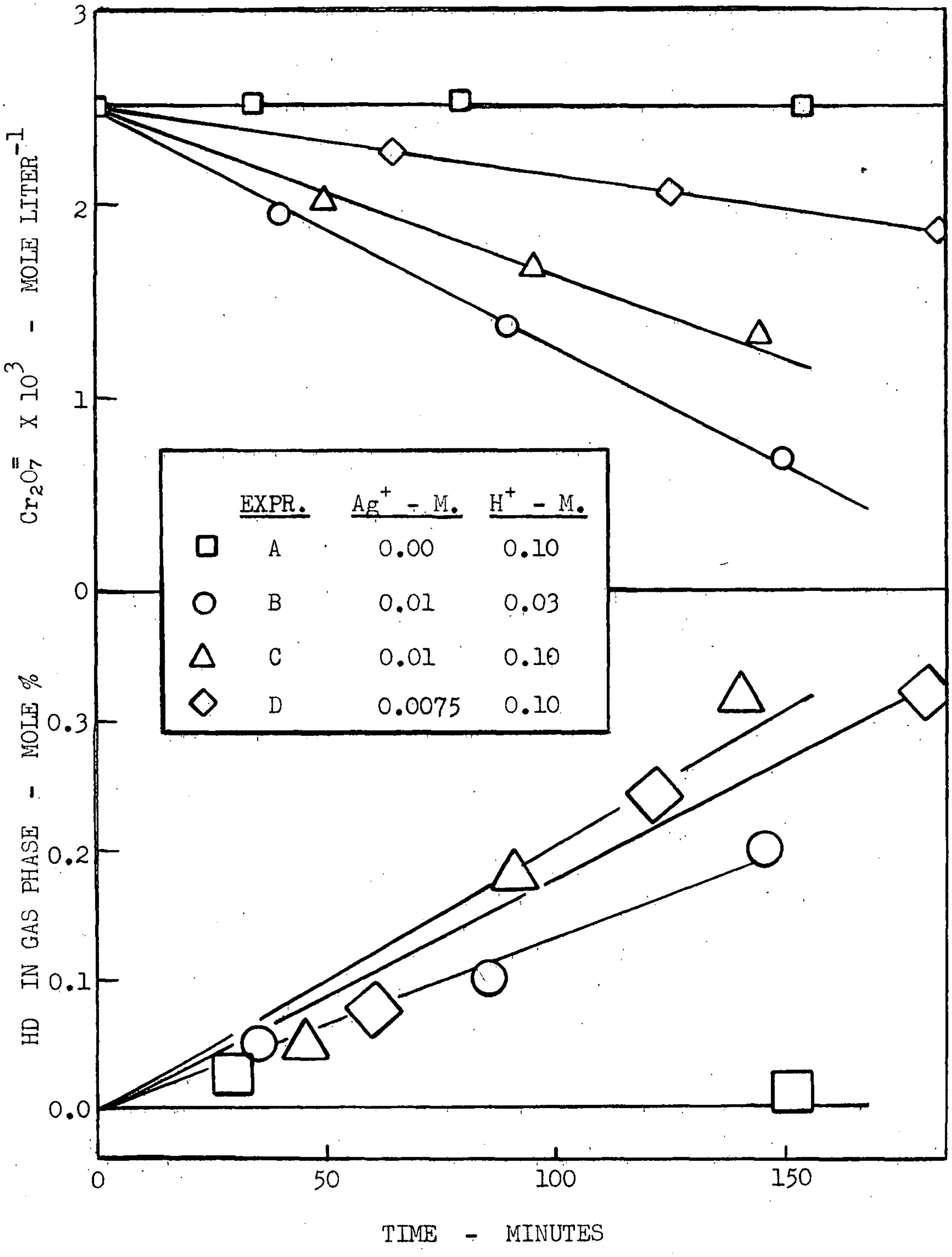


Fig. 27 Deuterium exchange and reduction of $Cr_2O_7^=$ in $D_2O$ enriched solutions. Temp. 110°C. Initial conditions: 4.0 atm. $H_2$, solution volume 3 liter, gas volume 1.74 liter. $D_2O$ content of solvent approx. 20 mole per cent.

Also, for a given acid concentration, the rate of exchange decreases, with decreasing silver ion concentration, less rapidly than the rate of reduction of $Cr_2O_7^=$. This is consistent with competition between $Ag^+$ and acid for an intermediate. Thus the results are in qualitative agreement with the postulated mechanism. Quantitatively, it would appear that the observed HD contents are low by a factor of 2; this factor would probably have been larger if data applicable to 110° could have been used in calculating "n".

An apparent discrepancy of this order could be accounted for on the basis of an isotope effect in the back reaction leading to the formation of HD, i.e. if, as might be expected for a proton transfer, $k^D_{-1} < k^H_{-1}$. No indication of such an isotope effect (except for experiment C) is, however, observed from the measured values of the rates of reduction of $Cr_2O_7^=$ (see Table XI (b) ). If $k^H_{-1}$ were greater than $k^D_{-1}$ the net rate of reaction in the deuterium enriched water would be greater than the rate in light water (assuming that the other rate constants are not affected by added $D_2O$). An isotope effect $(k^H_{-1}/k^D_{-1})$ of about 2 would result in an increase in the overall reduction rates of about 3%, 7%, and 10% for experiments B, C, and D, respectively. Since this is of the order of the experimental error (about ± 5% in the rate measurements) the results are inconclusive in this respect, and the possibility of an isotope effect cannot be rejected. Errors in gas sampling might also contribute to such a discrepancy if the diffusion of the HD to the exhaust valve of the autoclave were slow.

## C. SILVER PRECIPITATION FROM PERCHLORATE SOLUTION

In the previous sections a mechanism for the homogeneous activation of $H_2$ by $Ag^+$ ion was proposed on the basis of a kinetic study of the silver perchlorate catalysed reduction of dichromate. If a reducible substrate, such as dichromate, is not present, silver metal will be precipitated. In this section a brief examination of the kinetics of precipitation of silver from perchlorate solution at 110°C will be reported.

The reduction of $Ag^+$ by $H_2$ takes place according to the equation,

$$2\ Ag^+ + H_2 \longrightarrow 2\ Ag + 2\ H^+ \qquad \ldots\ldots (13)$$

Figure 28 shows the results of an experiment in which both the $Ag^+$ and $H^+$ ion concentrations were determined; the plot of $[Ag^+]$ against $[H^+]$ has a slope of +1 in accord with equation (13). Rate curves for the precipitation of silver under various conditions are shown in Fig. 29, while in Table XII observed and calculated rates are compared. The observed rates were determined by drawing tangents to the rate curves; this procedure is at best crude, giving errors of the order of ± 15%. For comparison, rates were calculated using equations (3) to (5) and the determined values of $k_I$, $k_{II}$, and $k'_{II}$; the acid concentrations used in these calculations were found from the initial concentrations with corrections applied for the acid produced during the course of the reaction. The rates of precipitation and of hydrogen activation (as measured by $Cr_2O_7^=$ reduction) follow the same trends, decreasing with increasing acid concentration. However, the calculated rates are in all cases higher (by about 20 to 60%) than the observed rates.

A rate curve for the reduction of dichromate followed by the precipitation of silver is shown in Fig. 30. No precipitation of the silver occurred until all of the dichromate had disappeared. It is seen that the rate of precipitation of silver is greater than the limiting reduction rate of

## TABLE XII

Comparison of observed rates of silver precipitation with rates calculated on the basis of the results of Section A.

$H_2$ Pressure, 4.0 atm.; Temp., 110ºC.

| Expr. | $[Ag^+] \times 10^2$ mole liter$^{-1}$ | $-d[Ag^+]/dt \times 10^6$ mole liter$^{-1}$ sec.$^{-1}$ obs. | calc. | calc./ obs. |
|---|---|---|---|---|
| A | 2.3 | 5.1 | 6.3 | 1.2 |
| | 1.4 | 2.0 | 3.0 | 1.5 |
| | 0.8 | 0.8 | 1.2 | 1.4 |
| B | 1.4 | 1.8 | 2.4 | 1.3 |
| | 0.95 | 0.9 | 1.2 | 1.3 |
| | 0.7 | 0.4 | 0.7 | 1.6 |
| C | 2.0 | 3.1 | 3.7 | 1.2 |
| | 1.4 | 1.7 | 2.0 | 1.2 |
| | 0.8 | 0.6 | 0.7 | 1.2 |
| D | 1.6 | 1.2 | 1.6 | 1.3 |
| | 1.2 | 0.7 | 0.9 | 1.3 |
| | 0.8 | 0.3 | 0.5 | 1.6 |

Initial conditions:

| Expr. | $AgClO_4 \times 10^2$ M. | $HClO_4$ M. |
|---|---|---|
| A | 2.48 | 0.003 |
| B | 1.54 | 0.031 |
| C | 2.61 | 0.031 |
| D | 1.73 | 0.102 |

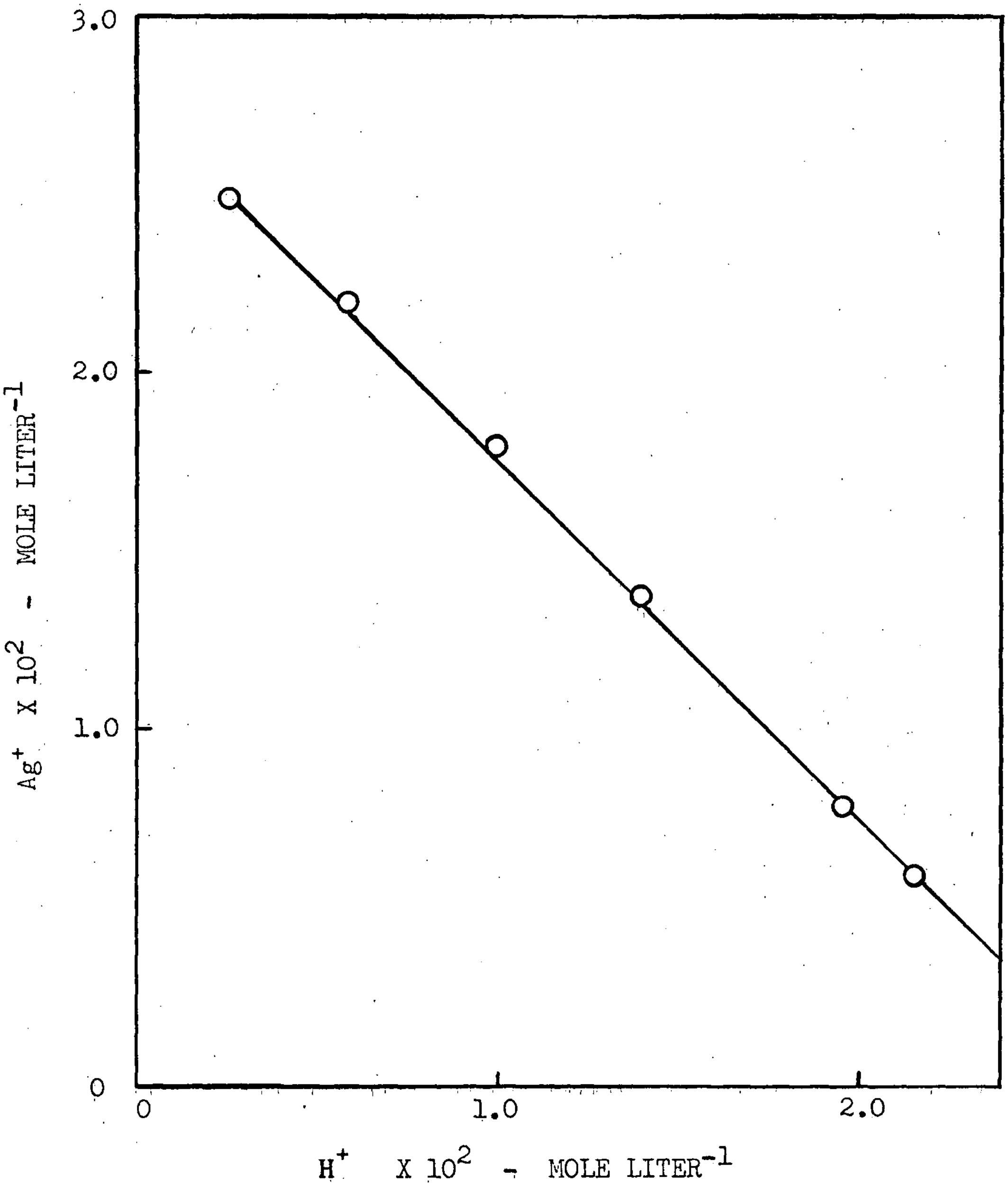


Fig. 28. Precipitation of silver from silver perchlorate solution. A plot of silver ion concentration against hydrogen ion concentration as determined at various times during the reaction. Solution 0.003 M. $HClO_4$ initially.

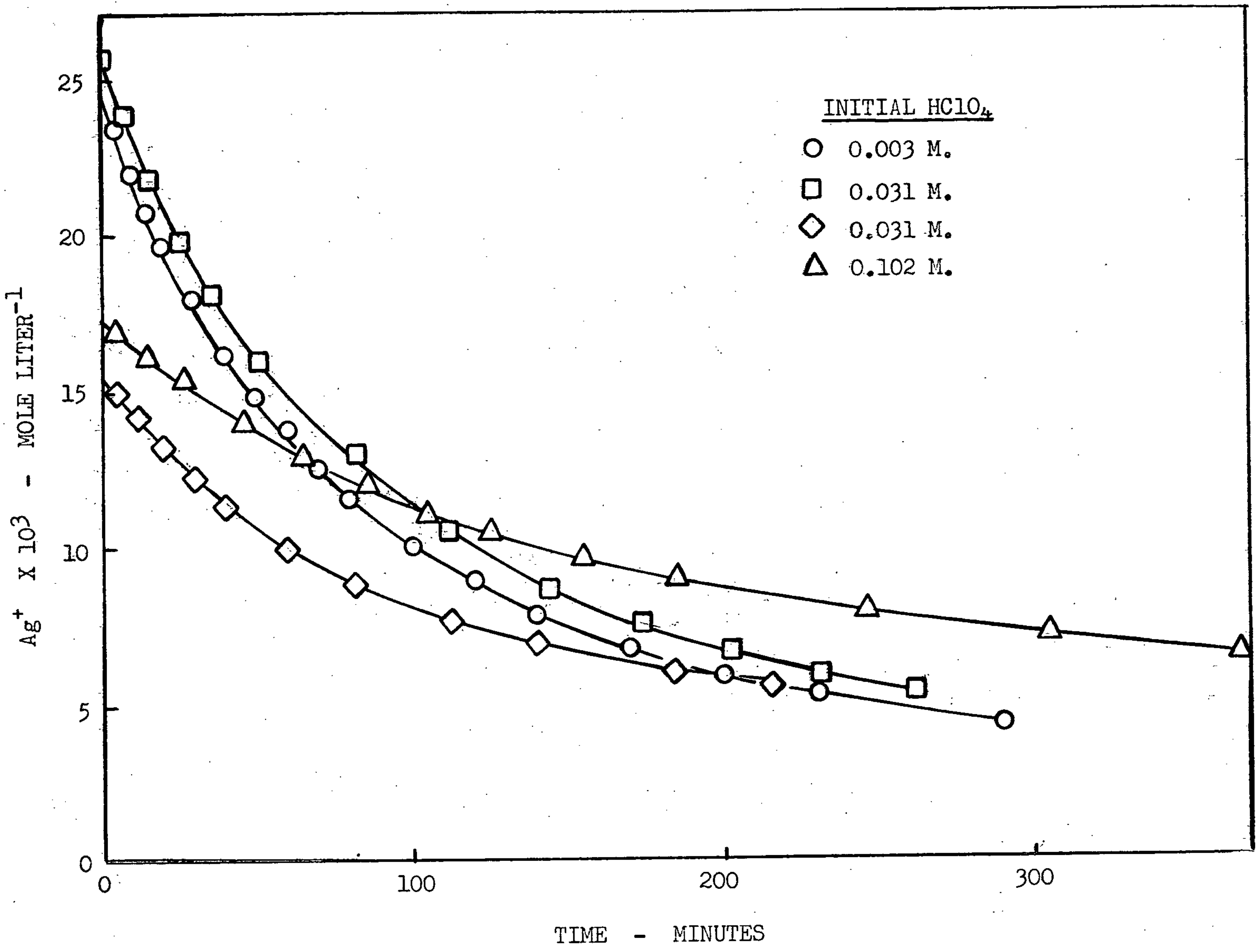


Fig. 29. Rate plots for the precipitation of silver from perchlorate solution. Temp. 110°C; $H_2$ pressure, 4.0 atm.

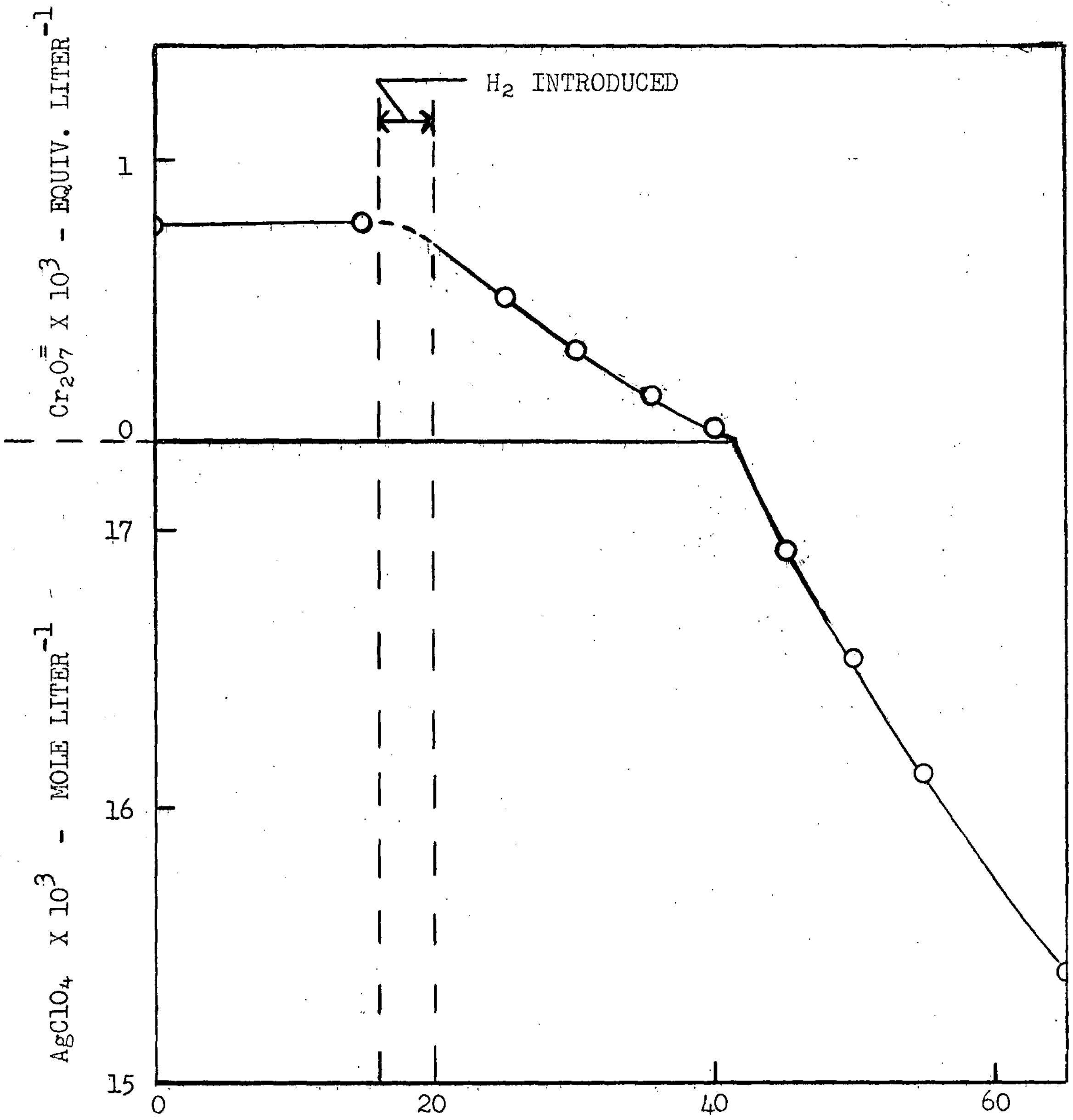


Fig. 30. Rate plot for dichromate reduction followed by silver precipitation. Initial solution composition: 0.77 X $10^{-3}$ equiv. liter$^{-1}$ $Cr_2O_7^{=}$; 17.3 X $10^{-3}$ M. $AgClO_4$; 0.102 M. $HClO_4$. $H_2$ pressure, 4.0 atm. Temp. 110°C.

dichromate as $[Cr_2O_7^=] \rightarrow 0$. This probably indicates that the reactive intermediates become stabilized on the surface of the silver crystals and do not participate in back reactions. The comparison of the observed and calculated rates indicates that this "stabilization" is not complete. It is apparent from Fig. 30 that any induction period, due to nucleation of the metallic phase, in the precipitation of silver must be very small.

The precipitate produced was identified as silver by X-ray diffraction (Appendix C). When formed in acid solution this precipitate consisted mainly of pellets about 0.5 to 2 mm. in diameter. These pellets, as shown by the photomicrographs in Appendix C, were composed of very small particles about 5 $\mu$ in diameter. The product from the solution initially 0.003 M. in $HClO_4$ formed principally as a sponge adhering to the walls and fittings of the autoclave.

The results of this cursory examination of the precipitation of silver are consistent with the view that both the precipitation reaction and the catalysed reduction of dichromate proceed by essentially the same mechanism. Complications in the case of the precipitation appear to arise from the presence of some back reaction, possibly similar to that observed in the reduction of $Cr_2O_7^=$ at low $Cr_2O_7^=$ concentration. The extent of this back reaction may be governed by the presence of silver crystals. Similar discrepancies between observed rates of metal precipitation and rates of activation of hydrogen have been found in the $Cu^{++} - H_2$ system (4).

## D. SILVER PRECIPITATION FROM SOLUTIONS CONTAINING COMPLEXES OF SILVER

In the cupric and mercuric systems (see Table III), large differences in rates of activation of hydrogen were observed between the simple hydrated ions and ions present as complexes (57, 61). In view of this behaviour, a brief examination of the reactivity of two different silver complexes was undertaken. Acetate and ethylene diamine complexes were chosen as representative of carboxylic acid and amine type compounds.

The activation of $H_2$ by the acetate complex could not be investigated by the dichromate method because of the insolubility of $AgCrO_4$ at acid concentrations where the silver acetate complex is stable. The reaction was followed, therefore, by observing the precipitation of silver. In the studies on the perchlorate solutions it was noted that the rate of reaction of hydrogen in the precipitation process was less than in the dichromate reduction. This discrepancy, if due to a back reaction, would probably not be so serious in the case of silver complexes with basic ligands on account of the proton stabilization.

## Acetate System

Rate plots for the precipitation of silver from solutions containing acetate are shown in Fig. 31; the plots indicate apparent first order behaviour to about 85% reaction. If it is assumed that the rates are proportional to the partial pressure of $H_2$, the rate equation becomes,

$$-\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[Ag(I)]}{dt} = k\,[Ag(I)][H_2] \qquad \ldots\ldots (14)$$

The results presented in Table XIII (a) indicate that no change in rate was produced by a three fold change in acetic acid concentration at constant NaOAc concentration. On the other hand an increase in the sodium acetate concentration produced a marked increase in rate. The rate constants determined at various NaOAc concentrations are plotted in Fig. 32.

The fine granular precipitate was identified as silver by X-ray diffraction.

## TABLE XIII

Precipitation of silver by hydrogen from solutions of silver complexes

(a) Acetate Complexes

Temp. 70°C.; Initial $AgClO_4$ $9.8 \times 10^{-3}$ M. Determinations at 4 atm. $H_2$

| HOAc<br>M. | NaOAc<br>M. | HOAc / NaOAc | k X $10^2$<br>$l.mole^{-1}sec.^{-1}$ | pH |
|---|---|---|---|---|
| 0.30 | 0.10 | 3 | 3.65 | 4.1 |
| 0.10 | 0.10 | 1 | 3.68 | 4.5 |
| 0.20 | 0.20 | 1 | 6.14 | 4.5 |
| 0.30 | 0.30 | 1 | 7.98 | 4.6 |
| $3.4 \times 10^{-5}$ | - | - | 0.80 | 6.0 - 5.0 * |

* Silver added as AgOAc.

(b) Ethylene Diamine Complexes

Temp. 70°C.; Initial $AgClO_4$ $1.2 \times 10^{-2}$ M.; Determinations at 4 atm. $H_2$

| EDA<br>M. | $EDA.HClO_4$<br>M. | NaOH<br>M. | k<br>$l.mole^{-1}sec.^{-1}$ | pH |
|---|---|---|---|---|
| 0.18 | 0.06 | - | 0.026 | 10.5 |
| 0.36 | 0.12 | - | 0.028 | 10.6 |
| 0.21 | - | 0.047 | 0.136 | - |
| 0.21 | - | 0.093 | 0.251 | - |

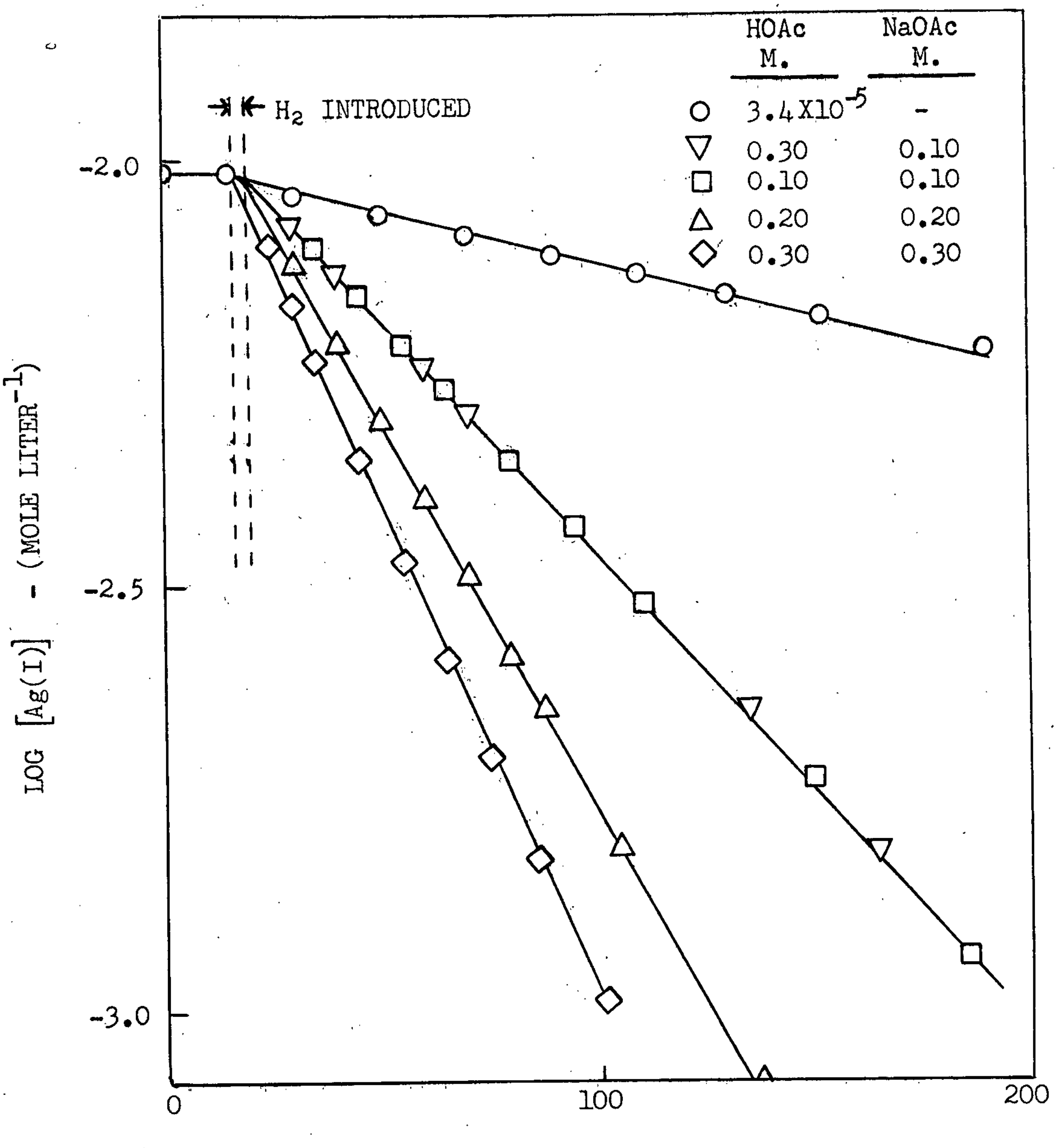


Fig. 31. Rate plots for the precipitation of silver from acetate solutions by reduction with hydrogen. Temp. 70°C; $H_2$ pressure, 4.0 atm.

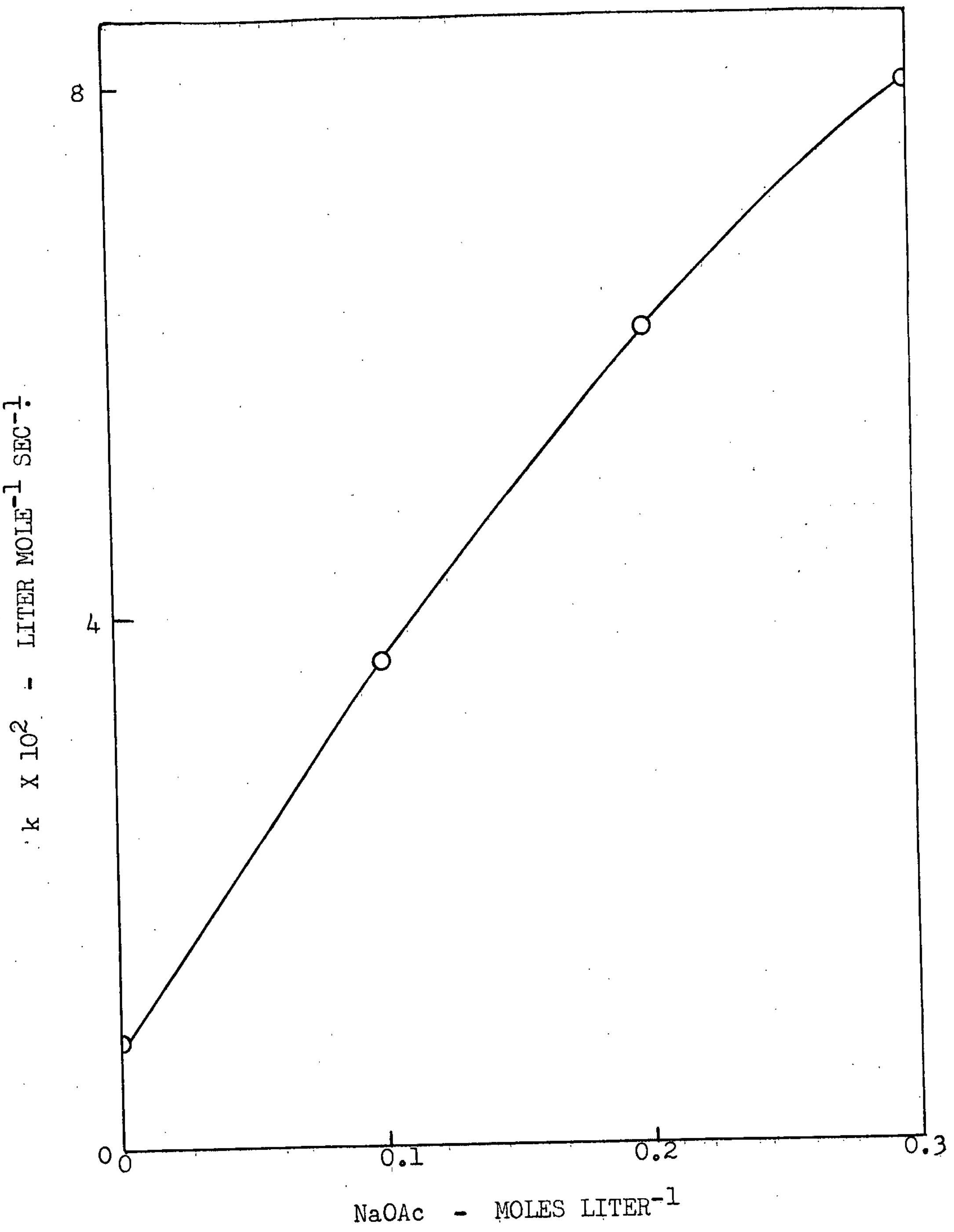


Fig. 32. Effect of sodium acetate on the rate of precipitation of silver by hydrogen. Temp. 70°C.

Any complete discussion of the kinetics would require a knowledge of the various species present in solution. Unfortunately silver acetate complexity constants have been determined only at room temperature, hence the following discussion can at best be only semi-quantitative. Furthermore, this room temperature data (91) indicates that the solutions studied all contained appreciable concentrations of at least two of $Ag^+$, AgOAc, and $Ag(OAc)_2^-$. However, even at the lowest acetate concentration used, it is probable that not more than 15% of the observed rate could be due to activation of $H_2$ by uncomplexed $Ag^+$. As the NaOAc concentration is increased, the formation of the complexed species is favoured; it may therefore be concluded that the reactivity of the silver acetate complexes is much higher than that of the uncomplexed silver ion. Using room temperature equilibrium data, k for the reaction of AgOAc was estimated as approximately $(9 \pm 2) \times 10^{-2}$ $l.mole^{-1}sec.^{-1}$ A similar accelerating effect due to acetate ligands was observed in the cupric system (56). In the silver system, as in the mercuric system (61), the reactivity of the diacetate complex seems to be greater than that of the monoacetate complex.

## Ethylene Diamine System

The reduction of the silver - ethylene diamine (EDA) complex proceeded with kinetics essentially first order in Ag(I), as the rate plots in Fig. 33 indicate. Second order rate constants, calculated assuming the rates to be proportional to hydrogen pressure, are given in Table XIII (b). It is seen that doubling the ethylene diamine concentration at constant pH produced only a small change in rate. Increasing the hydroxide ion concentration, however, produced a very marked increase in rate; the variation of the rate constant with NaOH concentration is shown in Fig. 34.

The precipitated product was identified as silver by X-ray diffraction. This precipitate was darker in colour than the precipitate from acetate solutions; it consisted of very fine particles, as indicated by the photomicrographs in Appendix C.

Room temperature complexity constants for the silver - ethylene diamine system (92) indicate that there is essentially complete complexing of the silver as $Ag(EDA)_2^+$ in the solutions considered here. Unlike the ethylene diamine complexes of cupric and mercuric ions, $Ag(EDA)_2^+$ is reduced more rapidly by hydrogen than the uncomplexed $Ag^+$ ion. This difference is possibly a reflection of the relatively lower stability of the silver complex; thus the strength of the metal ligand bond does not overcome the proton stabilizing effect of the amine. The hydroxyl ion acceleration of the reaction is similar to that observed in the mercuric - ethylene diamine system (61). In the case of cobalt amine complexes (93), an equilibrium of the type,

$$M\text{-}NH_3^{+n} + OH^- \rightleftharpoons M\text{=}NH_2^{+(n-1)} + H_2O$$

has been proposed to explain certain kinetic results. A similar equilibrium might account for the effect of $OH^-$ on the reaction rates of silver and mercuric amine complexes, on the grounds that $\bar{N}H(CH_2)_2NH_2$ would probably be a stronger base than $NH_2(CH_2)_2NH_2$.

The result of one experiment indicated that the $Ag(CN)_2^-$ complex is not reduced under 4 atm. $H_2$ at a measurable rate at 70°C. This inactivity may be attributed to the strong Ag-C binding, reflected in the high stability of this complex.

Some results have been reported for the reduction of silver sulphate (73) which indicate that a reaction first order in Ag(I) takes place, as observed here for acetate and EDA complexes. However, the $H_2$ pressure dependence was given as $(P_{H_2}^{0.5} - 2.25)$ and an induction period was noted. The former effect may have been due to catalysis by the Pt electrodes present in the solution for conductivity measurements.

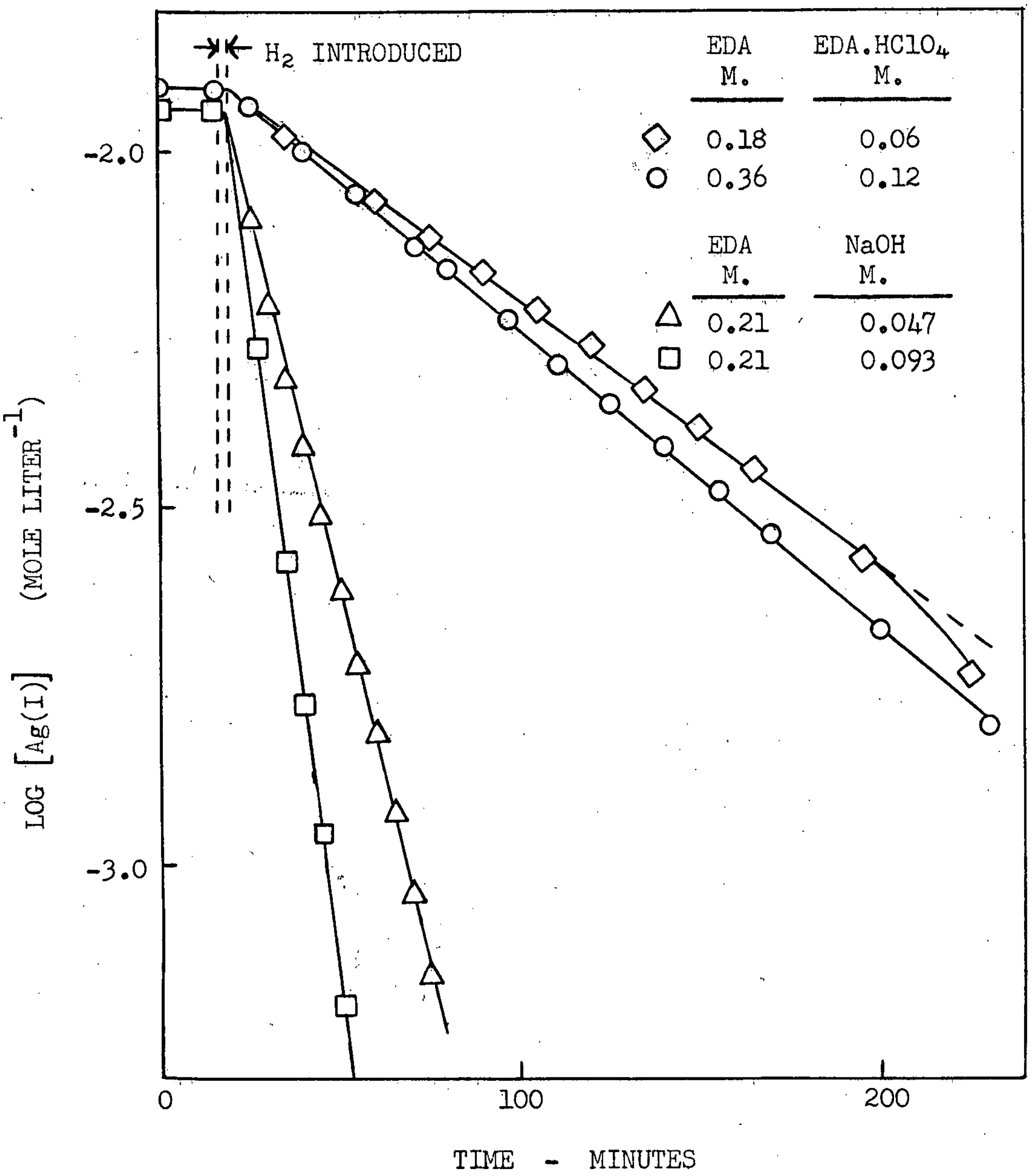


Fig. 33. Rate plots for the reduction of silver from solutions containing ethylene diamine. Temp. 70°C. $H_2$ pressure, 4.0 atm.

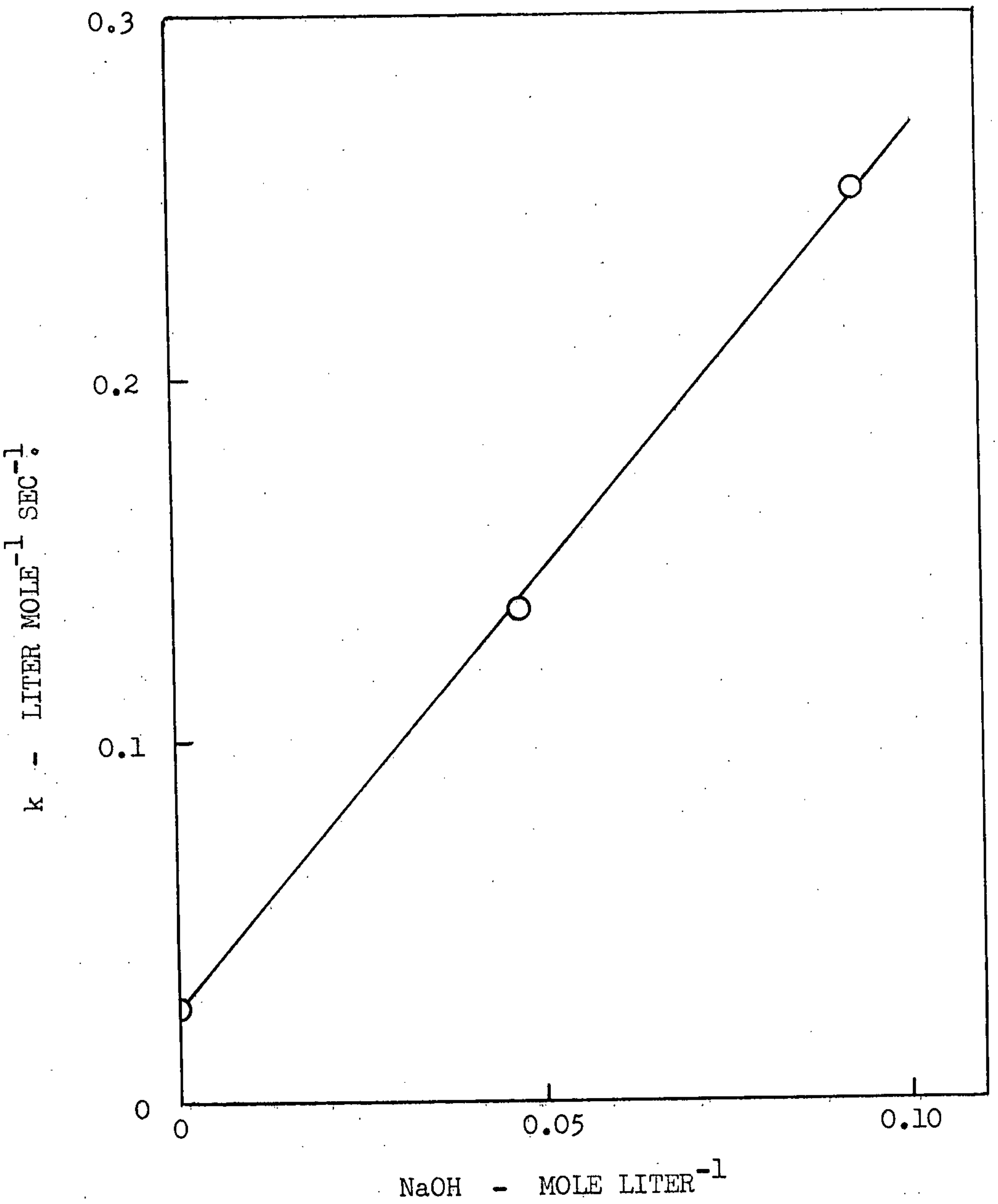


Fig. 34. Effect of NaOH on the rate of precipitation of silver from silver - ethylene diamine complexes. Temp. 70°C.

# PART II - REDUCTION OF PERMANGANATE BY MOLECULAR HYDROGEN

## EXPERIMENTAL

Most of the reagents used were described in Part I. Perchlorate salts were obtained from the G.F. Smith Co. Vanadyl perchlorate was prepared from perchloric acid and sodium vanadate; thallium (III) perchlorate solution was prepared from thallium (I) nitrate by oxidation with $NaBrO_3$, precipitation as hydroxide, and solution in perchloric acid. $KMnO_4$ solutions were prepared in the customary manner by boiling and filtering through glass wool.

The apparatus used for the low temperature silver catalysed dichromate reduction work was employed in the permanganate study. It was established that the reaction rate was independent of $H_2$ flow rates from 0.3 to 0.6 liter $min.^{-1}$ Solution concentrations of hydrogen were estimated as described in Part I.

In acid solutions, $MnO_2$ was found to be the only product of reduction in the presence of $MnO_4^-$. To follow the reaction, samples of the solution (after removal of the precipitated $MnO_2$ by centrifuging) were analysed for $MnO_4^-$ by adding an aliquot of standard ferrous ammonium sulphate solution and back titrating with $KMnO_4$. In a few experiments the $MnO_4^-$ was determined spectrophotometrically (using the 526 m$\mu$ peak); the rates determined by the two methods were in good agreement (see Table XIV). To determine experimentally the apparent valence of the manganese product, $H_2$ was passed through a known volume of solution, without removing any samples, until the reduction of $MnO_4^-$ was just complete. The whole reaction mixture (including the precipitated product) was added to a known volume of standard ferrous solution, and the excess ferrous content was determined by titration with $KMnO_4$. The apparent valence of the manganese product was thus found to be 4.0 for both the uncatalysed and silver catalysed reactions. When reduction was continued beyond the disappearance of the permanganate in the presence of $AgClO_4$, the apparent valence of the manganese fell to 3.0.

The reduction of $MnO_4^-$ in initially neutral solutions also yielded $MnO_2$ as the only product. The pH of such solutions rose slightly as a result of the reaction, but not sufficiently to permit the formation of detectable amounts of $MnO_4^=$. This was demonstrated by an experiment in which the samples were acidified (to decompose any $MnO_4^=$) before centrifuging; the observed rate agreed with the rates determined by the usual procedure (Table XV). With solutions containing added electrolyte (e.g. $NaClO_4$) the same analytical procedure as for acid solution was employed to follow the reaction. In the absence of an added electrolyte, the $MnO_2$ product remained uniformly dispersed in the solution as a colloidal suspension. The reaction was then followed by determining the total oxidizing capacity of the suspension (using standard ferrous solution), assuming the manganese to be present as a mixture of $MnO_4^-$ and $MnO_2$. Using the same procedure as for acid solutions the apparent valence of the manganese product was found experimentally to be 4.0.

In basic solution (containing initially from 0.3 to 0.6 M. NaOH), $MnO_4^-$ was reduced to $MnO_4^=$ which was stable and remained in solution. Manganese dioxide began to form only after this reduction had proceeded to the extent of about 85%. The reaction was usually followed by determining the decrease in total oxidizing capacity of the solution volumetrically, assuming all the manganese to be present as $MnO_4^-$ and $MnO_4^=$. The results obtained were in agreement with those obtained by an alternative procedure in which $MnO_4^-$ alone was determined following precipitation of the $MnO_4^=$ with $Ba^{++}$. Spectra of a basic solution before reduction and after 95% reduction are shown in Fig. 35; these spectra are of the form reported for permanganate and manganate, respectively (94). Measured rate constants were generally reproducible to within ± 5% for the uncatalysed reaction and to within ± 7% for the silver catalysed reaction.

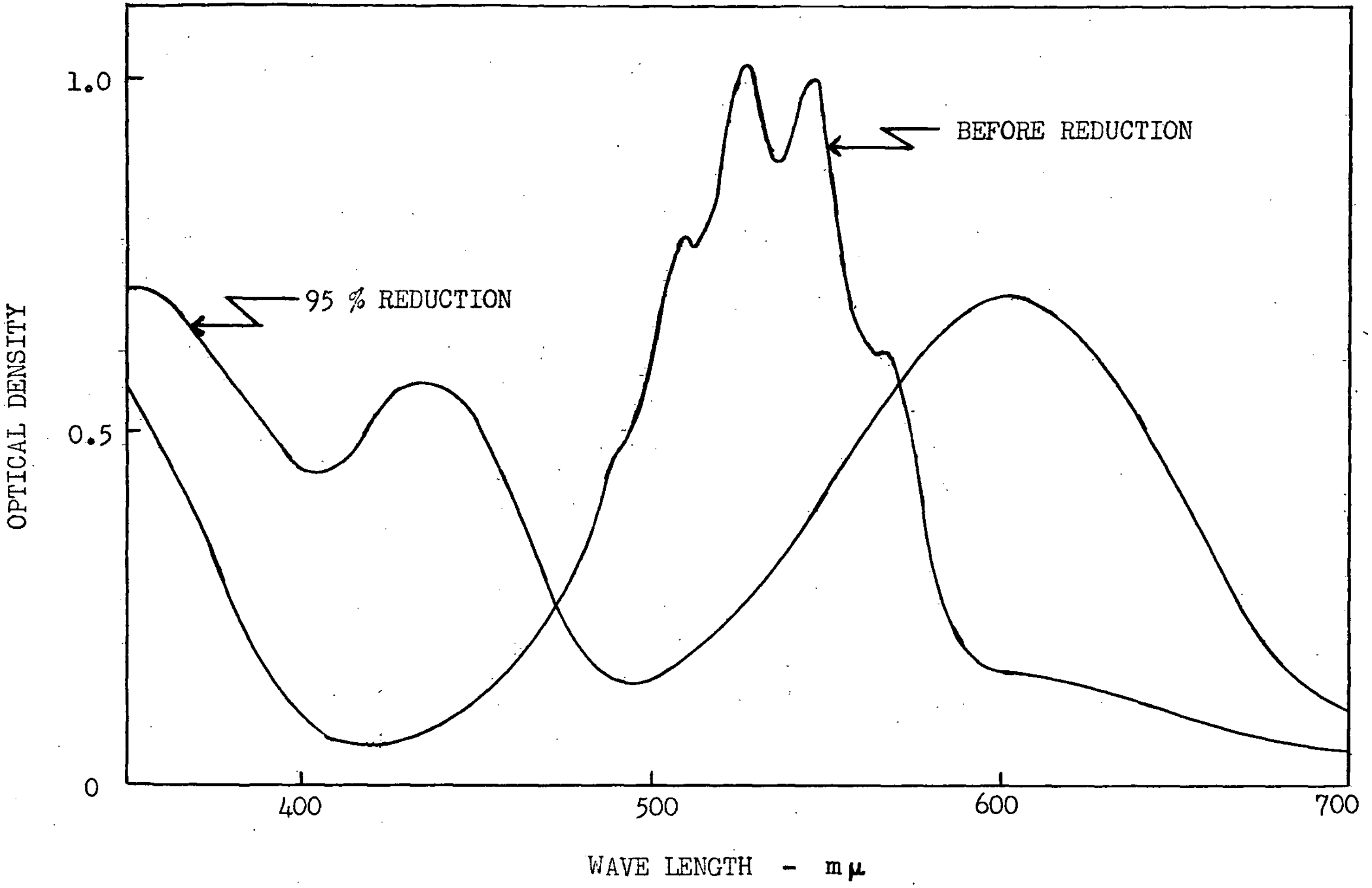


Fig. 35. Absorption spectra of a basic $KMnO_4$ solution before and after reduction by hydrogen. Initial solution composition: $4.0 X 10^{-3}$ M. $MnO_4^-$ ; $0.4 X 10^{-3}$ M. $MnO_4^=$; 0.30 M. NaOH. Samples diluted 10 X with 0.3 M. NaOH solution for spectral determinations.

## RESULTS AND DISCUSSION

### Reaction in Acid Solution

In keeping with the observation that $MnO_2$ is the only reduction product, it is concluded that the stoichiometry of the reaction between $MnO_4^-$ and $H_2$ in acid solutions is represented by the equation,

$$2\ MnO_4^- + 3\ H_2 + 2\ H^+ \longrightarrow 2\ MnO_2 + 4\ H_2O \qquad \ldots\ldots\ (15)$$

Possible complications might have arisen due to the competing spontaneous decomposition of $MnO_4^-$, i.e.

$$4\ MnO_4^- + 4\ H^+ \longrightarrow 4\ MnO_2 + 3\ O_2 + 2\ H_2O \qquad \ldots\ldots\ (16)$$

which is known to occur in acid solutions especially in the presence of $MnO_2$ which acts as a catalyst. However, this reaction was found to be negligibly slow compared with the reduction of $MnO_4^-$ by $H_2$ under the experimental conditions employed. No spontaneous decomposition of $MnO_4^-$ was detected prior to the introduction of $H_2$ in any of the experiments. Furthermore it was found, in an experiment at 0.3 M. $HClO_4$, that even after 60% of the $MnO_4^-$ initially present had been reduced by $H_2$ to $MnO_2$ (which was allowed to remain in contact with the solution) the apparent rate of spontaneous decomposition of $MnO_4^-$ under $N_2$ was only about 2% of its rate of reaction with $H_2$ under the same conditions. The effect was therefore neglected.

At constant temperature and $H_2$ partial pressure, the rate of reaction between $MnO_4^-$ and $H_2$ was found to be first order in $MnO_4^-$, as shown by the rate plots in Fig. 36. Furthermore, reference to Fig. 37 will indicate that the slopes of these plots are directly proportional to the partial pressure of $H_2$, and hence to the concentration of $H_2$ in solution. The reaction, therefore, appears to be second order.

## TABLE XIV

Reduction of permanganate by hydrogen in acid solution at 50°C.

| Initial $KMnO_4$ X $10^3$ M. | $HClO_4$ M. | $NaClO_4$ M. | k liter $mole^{-1}$ $sec.^{-1}$ |
|---|---|---|---|
| 4.1 | 0.3 | - | 0.82 |
| 2.0 | 0.3 | - | 0.82 |
| 0.8 | 0.3 | - | 0.83 |
| 0.4 | 0.3 | - | 0.92 (a) |
| 2.0 | 0.3 | - | 0.78 (b) |
| 1.9 | 0.3 | - | 0.81 (c),(d) |
| 2.2 | 0.3 | - | 0.80 (e) |
| 2.0 | 0.3 | - | 0.82 (a) |
| 2.0 | 0.3 | - | 0.98 (f) |
| 2.2 | 0.1 | 0.9 | 0.72 |
| 2.2 | 0.3 | 0.7 | 0.75 |
| 2.2 | 0.5 | 0.5 | 0.81 |
| 2.2 | 0.7 | 0.3 | 0.88 |
| 2.2 | 1.0 | - | 0.97 |
| 2.2 | 0.3 | 0.2 | 0.79 |
| 2.1 | 0.3 | 0.5 | 0.78 |
| 2.2 | 0.3 | 0.8 | 0.76 |
| 2.1 | 0.3 | 1.1 | 0.77 |
| 2.2 | 0.3 | 1.4 | 0.77 |

(a) Pyrex glass wool added to reaction vessel.
(b) $H_2$ flow rate 0.2 l. $min.^{-1}$
(c) $H_2$ flow rate 0.6 l. $min.^{-1}$
(d) Analysis by spectrophotometric method.
(e) Analysis by volumetric method.
(f) 0.004 mole $l.^{-1}$ $MnO_2$ added initially.

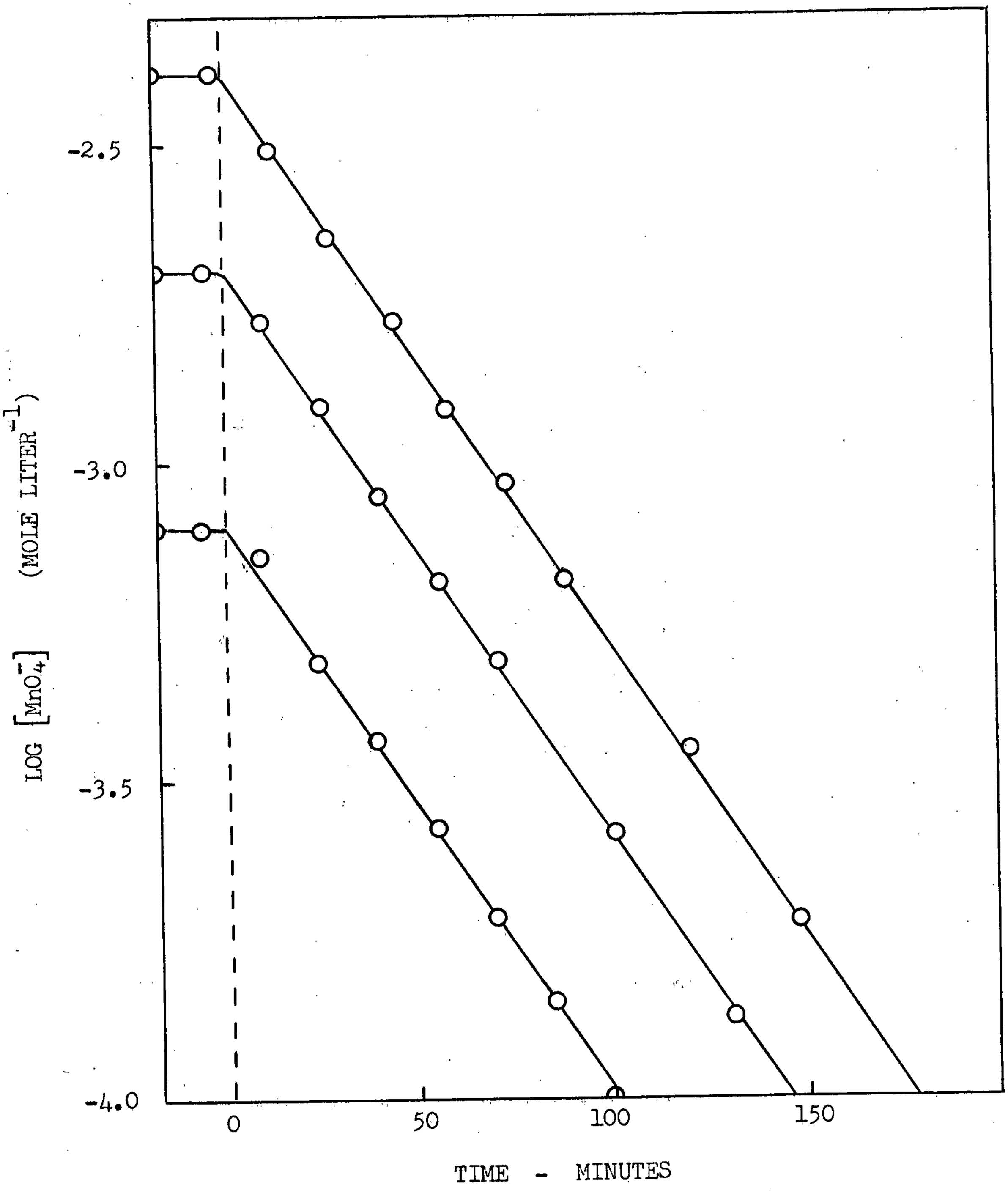


Fig. 36. Typical rate plots for the reduction of permanganate by by hydrogen in acid solution. Solutions 0.3 M. $HClO_4$; Temp. 50°C. $H_2$ partial pressure, 0.88 atm.

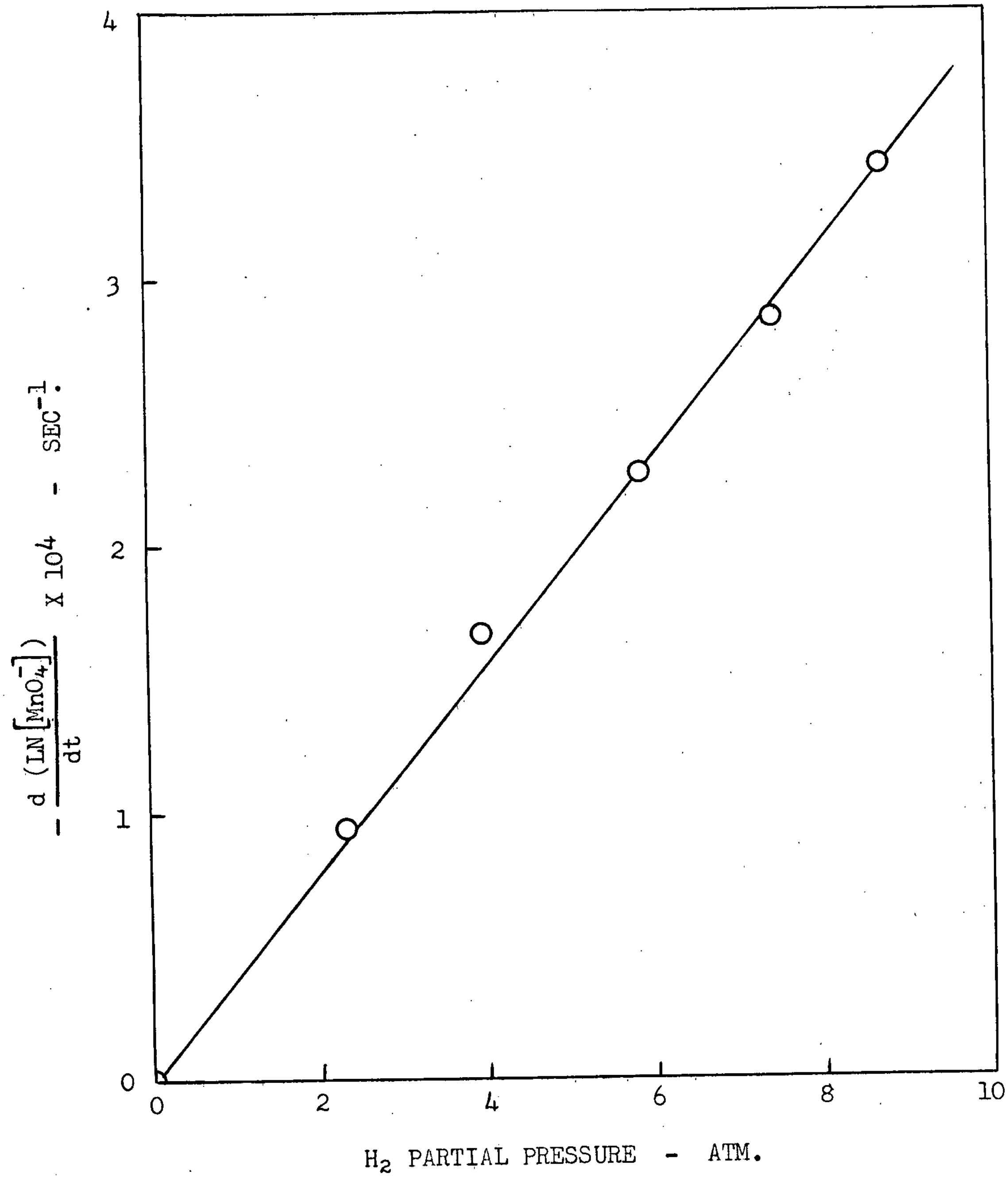


Fig. 37. Dependence of the rate of reduction of permanganate on $H_2$ pressure. Solutions 0.3 M. $HClO_4$. Temp. 50°C.

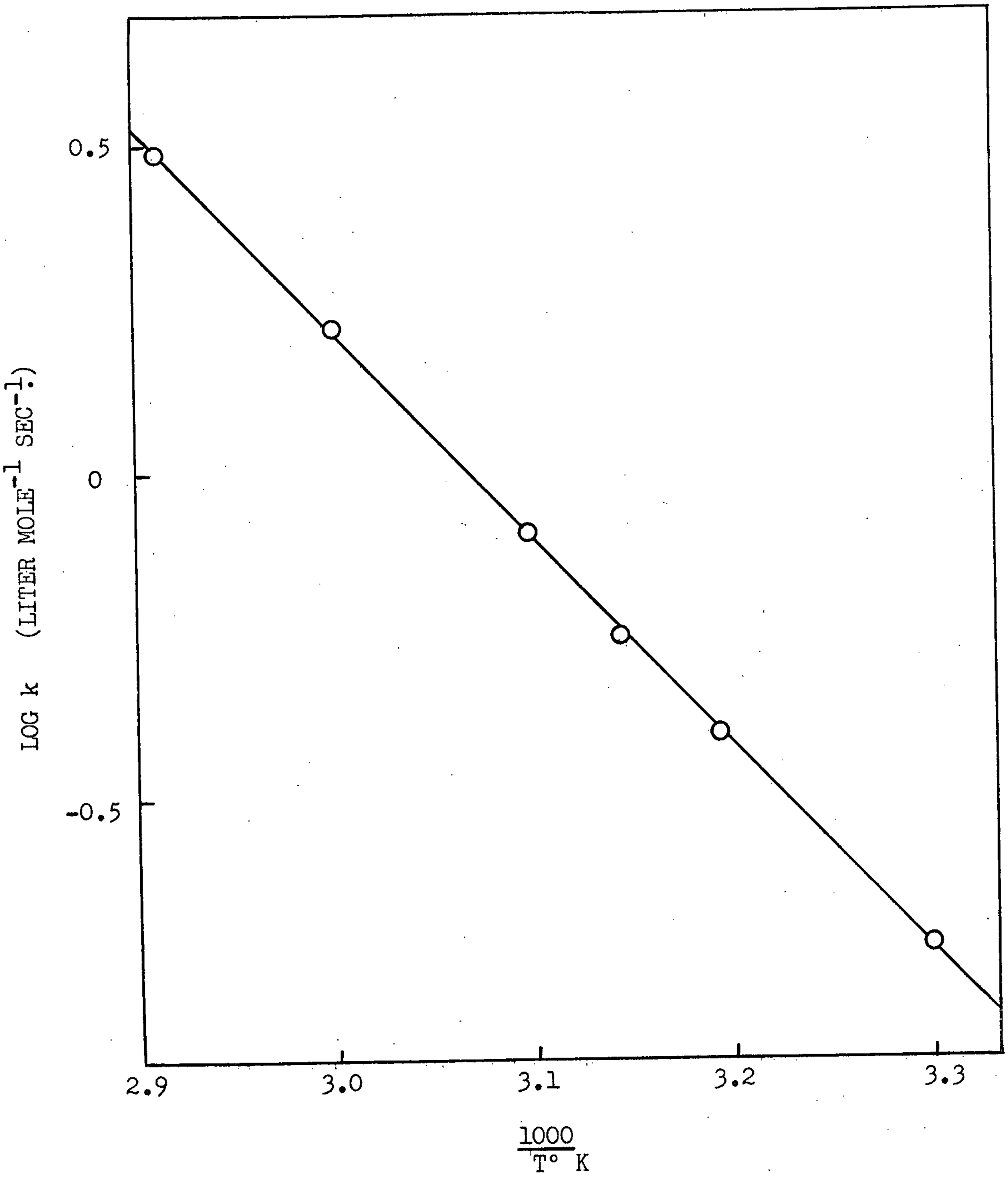


Fig. 38. Arrhenius plot for the reduction of permanganate by hydrogen in 0.3 M. $HClO_4$.

The convention, adopted in Part I, of expressing the rate laws in terms of the rate of reaction of hydrogen will also be employed here. Hence, using the known stoichiometry of the reaction, the rate equation becomes,

$$-\frac{d[H_2]}{dt} = -1.5\frac{d[MnO_4^-]}{dt} = k[H_2][MnO_4^-] \qquad \ldots\ldots (17)$$

Values of k, determined from the slopes of the apparent first order plots by means of equation (17) were substantially unaffected by variations in the initial $KMnO_4$ concentration between 0.0008 and 0.004 M., and by the addition of up to 1.4 M. $NaClO_4$. On the other hand, k increased slightly as the $HClO_4$ concentration was raised from 0.1 to 1.0 M. (see Table XIV).

The results in Table XIV also provide evidence for the homogeneous character of the reaction. Packing the reaction vessel with Pyrex glass wool did not increase the rate significantly. The addition of 0.004 mole liter$^{-1}$ $MnO_2$ to a solution containing 0.002 M. $MnO_4^-$ increased the apparent rate by only about 20%, suggesting that the $MnO_2$ normally formed during the reaction would have only a small effect, especially during the initial stages of the reaction. This is in accord with the fact that no significant deviations from linearity of the first order rate plots were generally observed until after at least 90% of the $MnO_4^-$ initially present had been reduced (see Fig. 36).

Values of k, determined at various temperatures from 30° to 70°C gave the Arrhenius plot shown in Fig. 38 . This plot was fitted by the equation,

$$k = 4.2 \times 10^9 \exp[(-14700 \pm 500)/RT] \text{ l. mole}^{-1}\text{sec.}^{-1}$$

with $\Delta H^{\ddagger} = 14 \pm 0.5$ kcal.mole$^{-1}$ and $\Delta S^{\ddagger} = -17 \pm 2$ cal. deg.$^{-1}$mole$^{-1}$.

## Reaction in Neutral Solution

The reaction between $MnO_4^-$ and $H_2$ in neutral solution may be represented as,

$$2\ MnO_4^- + 3\ H_2 \longrightarrow 2\ MnO_2 + 2\ H_2O + 2\ OH^-\ .$$

The kinetics were found to be of first order in permanganate concentration in agreement with the results reported by Just and Kauko (63). The rate constants reported by these authors at 6°, 15°, and 25°C were extrapolated to 50°C to give a value of $k = 0.76$ l. mole$^{-1}$sec.$^{-1}$, about 20% higher than the result reported here.

The values of k given in Table XV indicate that the rate in neutral solution was about 15% lower than in weakly acid solution and was unaffected by the addition of up to 1 M. $NaClO_4$.

## Reaction in Basic Solution

In solutions containing 0.3 and 0.6 M. NaOH, the initial reaction between $MnO_4^-$ and $H_2$ was found to be

$$2\ MnO_4^- + H_2 + 2\ OH^- \longrightarrow 2\ MnO_4^= + 2\ H_2O \qquad \text{......}\ (18)$$

Rate plots depicting the changing concentrations of $MnO_4^-$ and $MnO_4^=$ are shown in Fig. 39. The total manganese concentration in solution does not begin to fall off, due to the formation of $MnO_2$, until about 80% of the $MnO_4^-$ initially present is reduced to $MnO_4^=$. The altered stoichiometry of the reaction required the use of a different equation to relate the rate of reaction of $H_2$ to the measured rate of disappearance of $MnO_4^-$, i.e.,

$$-\frac{d[H_2]}{dt} = 0.5\ \frac{d[MnO_4^-]}{dt} = k\ [H_2][MnO_4^-] \qquad \text{......}\ (19)$$

Otherwise, the kinetics are apparently of the same form as in acid solution (equation (17) ), assuming the rate to be proportional to the hydrogen pressure. The values of k listed in Table XVI are seen to be of the same

## TABLE XV

Rates of reduction of permanganate by hydrogen in neutral solution

| Temp. °C | $NaClO_4$ M. | k $l.mole^{-1}sec.^{-1}$ |
|---|---|---|
| 50 | - | 0.62 |
| 50 | 0.3 | 0.64 |
| 50 | 1.0 | 0.62 |
| 50 | 0.3 | 0.61 * |
| 40 | 0.3 | 0.31 |

* Samples acidified to decompose any $MnO_4^=$ before centrifuging.

## TABLE XVI

Rates of reduction of permanganate by hydrogen in basic solution

| Initial $KMnO_4 \times 10^3$ M. | NaOH M. | $NaClO_4$ M. | Temp. °C | k $l.mole^{-1}sec.^{-1}$ |
|---|---|---|---|---|
| 4.1 | 0.3 | - | 40 | 0.32 |
| 8.0 | 0.3 | - | 40 | 0.33 |
| 15.4 | 0.3 | - | 40 | 0.32 |
| 3.8 | 0.3 | - | 40 | 0.33 (a) |
| 4.1 | 0.3 | - | 40 | 0.32 (b) |
| 4.0 | 0.6 | - | 40 | 0.33 |
| 4.0 | 0.3 | - | 50 | 0.67 |
| 3.9 | 0.6 | 0.4 | 50 | 0.69 |
| 1.7 | 0.3 | 0.7 | 50 | 0.70 |

(a) Both $MnO_4^-$ and $MnO_4^=$ determined.

(b) $Ba(ClO_4)_2$ added to solution.

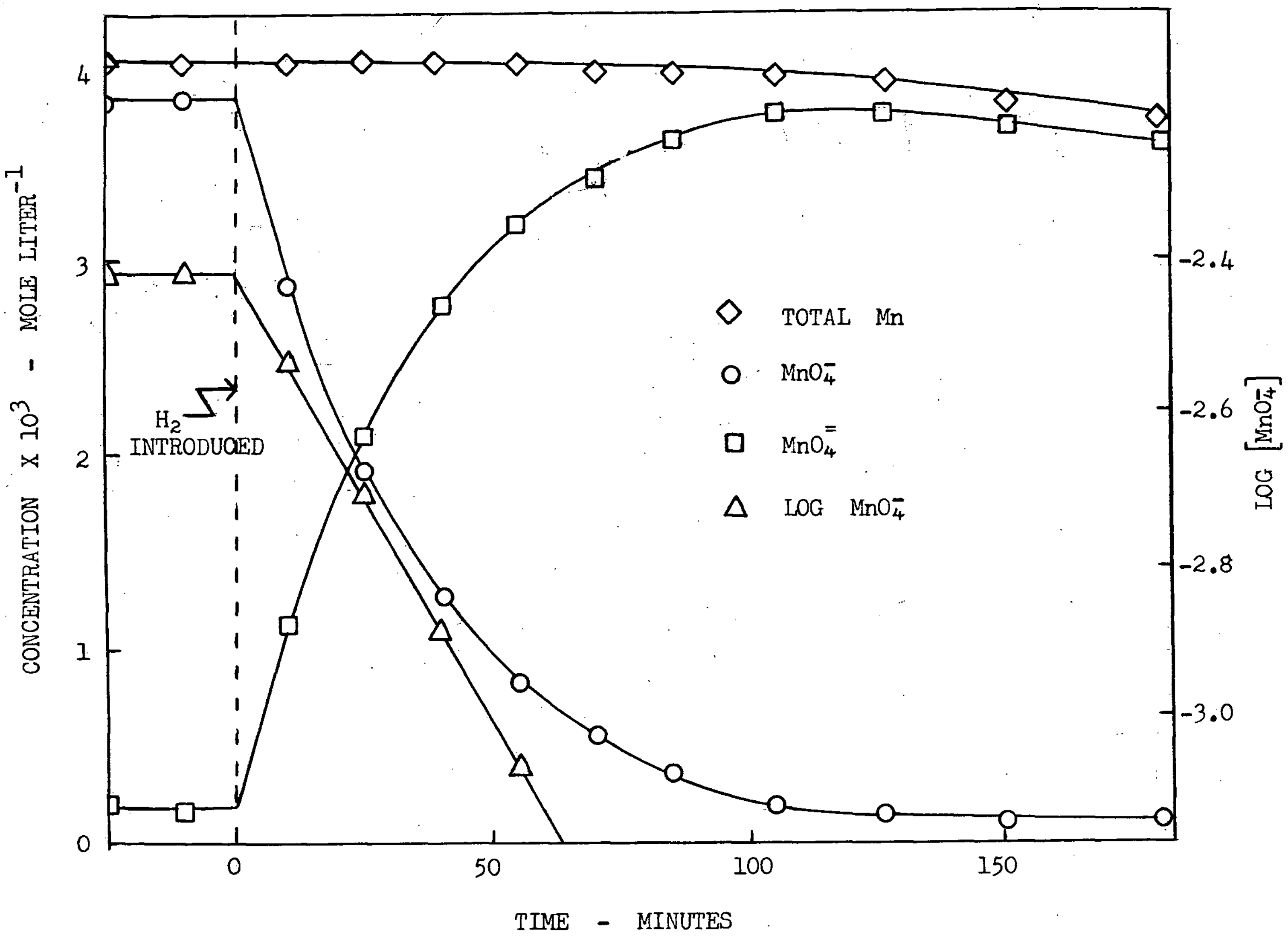


Fig. 39. Rate plots for the reduction of permanganate by hydrogen in 0.3 M. NaOH at 40°C; $H_2$ pressure, 0.93 atm. Manganate and permanganate both determined.

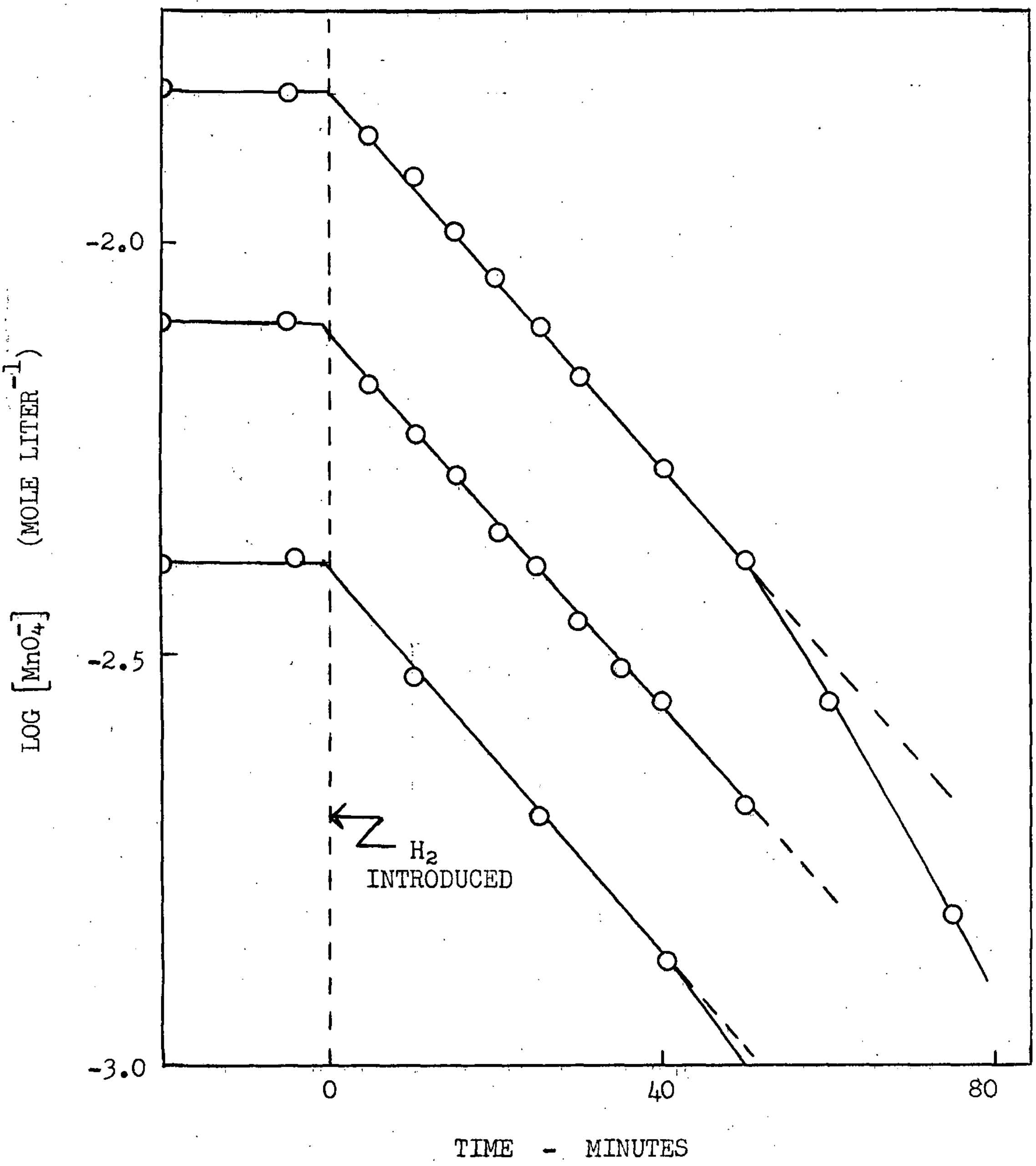


Fig. 40. Rate plots for the reduction of permanganate by hydrogen in 0.3 M. NaOH at 40°C. $H_2$ pressure, 0.92 atm. Total oxidizing capacity of the solutions determined; manganese assumed to be present as $MnO_4^-$ and $MnO_4^=$ only.

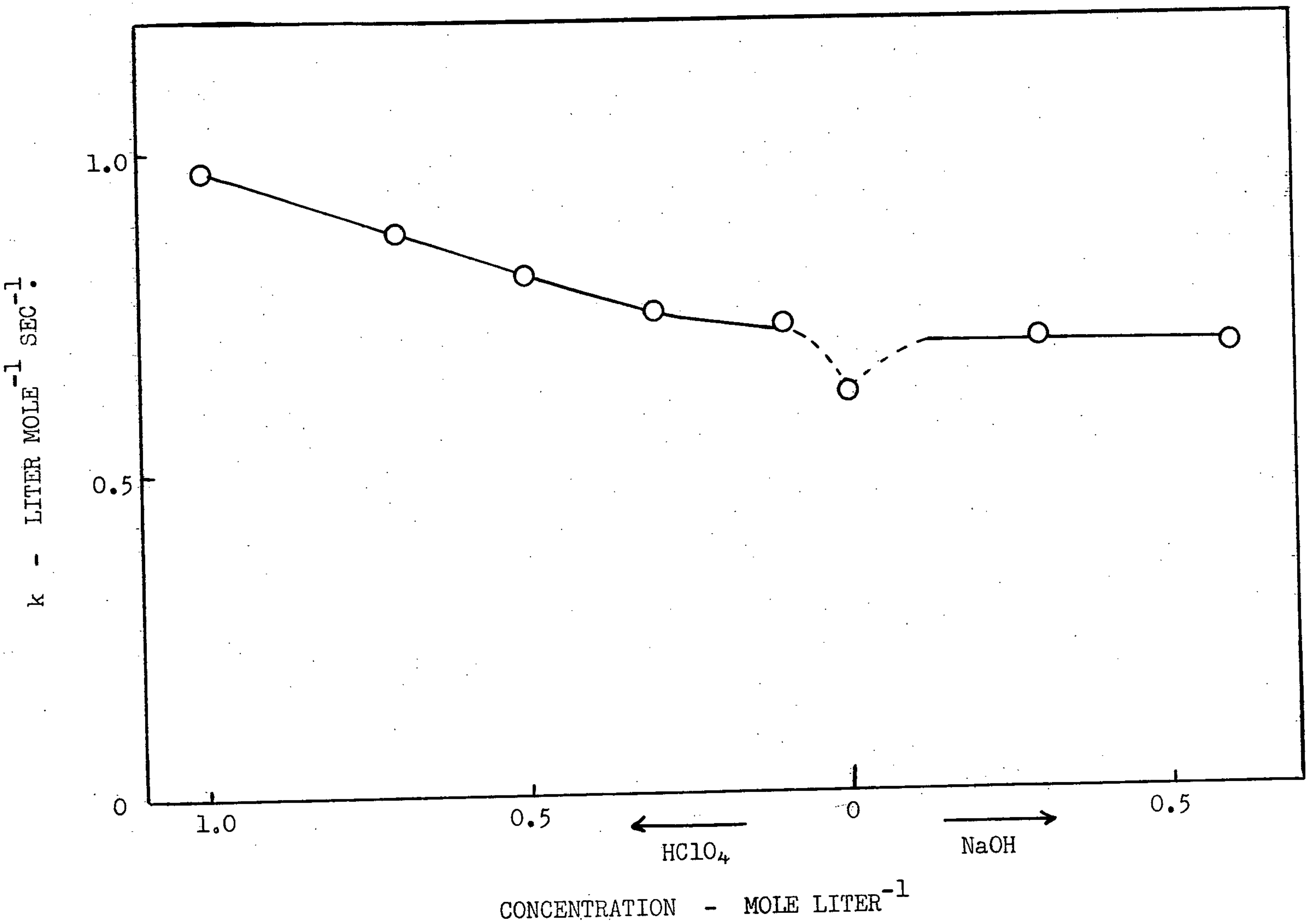


Fig. 41. Effect of acid and base on the rate of reduction of permanganate by hydrogen at 50°C.

order as those for neutral and acid solutions and to be unaffected by variations in initial $MnO_4^-$ concentration, NaOH concentration, and by the addition of up to 0.7 M. $NaClO_4$.

The fact that the first order plots (Fig. 40) are consistently linear to at least 70% reaction suggests that the $MnO_4^=$ produced in the reaction does not contribute appreciably to the activation of $H_2$. This conclusion is also supported by the results of an experiment (Table XVI) in which excess $Ba(ClO_4)_2$ was added initially to the solution to precipitate the $MnO_4^=$ product as it formed during the reaction. The rate was the same as in the absence of $Ba^{++}$.

No kinetic measurements were made at $OH^-$ concentrations above 0.6 M. because of the increasing instability of $MnO_4^-$ under these conditions.

Throughout the pH range investigated (1.0 $H^+$ to 0.6 M. NaOH) the kinetics of the uncatalysed reaction were represented essentially by equations (17) and (19). The measured values of k, plotted in Fig. 41, varied slightly over this range. The predominant trend was for k to increase with increasing acidity, but the variation was not sufficient to indicate a significant change in mechanism.

### Effect of Added Salts on the Reaction in Acid Solution

Several salts were tested for possible catalytic or inhibitory influences on the reaction in acid solution (Table XVII). The additions of $Cu(ClO_4)_2$, $Co(ClO_4)_2$, $VO_2ClO_4$, and $Tl(ClO_4)_3$ were without significant effect on the rate. In the presence of 0.3 M. NaF, the apparent rate, following a short induction period, was about 10% faster than normal; this may be due to the temporary formation of a complex between Mn(IV) and $F^-$ which subsequently decomposes to $MnO_2$. The addition of $Fe(ClO_4)_3$ caused a small increase in the apparent rate which could be traced, in part,

## TABLE XVII

Effect of various salts on the rate of reduction of permanganate by hydrogen in acid solution

| Temp. °C | $HClO_4$ M. | Added Salt | k $l.mole^{-1}sec.^{-1}$ |
|---|---|---|---|
| 40 | 0.3 | - | 0.40 |
| 40 | 0.3 | 1.0 M. $Cu(ClO_4)_2$ | 0.36 |
| 40 | 0.3 | 0.2 M. $Co(ClO_4)_2$ | 0.40 |
| 40 | 0.3 | 0.05 M. $VO_2ClO_4$ | 0.40 |
| 40 | 0.3 | 0.37 M. $Fe(ClO_4)_3$ | 0.50 |
| 40 | 0.3 | 0.04 M. $Hg(ClO_4)_2$ | 0.62 * |
| 40 | 0.3 | 0.02 M. $AgClO_4$ | 1.40 |
| 40 | 1.28 | - | 0.49 |
| 40 | 1.33 | 0.03 M. $Tl(ClO_4)_3$ | 0.47 |
| 50 | 0.3 | - | 0.82 |
| 50 | 0.3 | 0.3 M. NaF | 0.89 |

* k calculated from rate at $MnO_4^- = 2.2 \times 10^{-3}$ M.

to an induced decomposition of $MnO_4^-$ rather than to catalysis of the reaction with $H_2$. The small effect on the hydrogenation itself was not reproducible and may have been caused by colloidal ferric hydroxide. $Hg(ClO_4)_2$ exhibited a small catalytic effect on the reaction whose magnitude was of the order expected on the basis of previous measurements of the rate of activation of $H_2$ by $Hg^{++}$ (60) (see Table II). The mechanism of the catalysed reaction is probably,

$$Hg^{++} + H_2 \longrightarrow Hg + 2\,H^+ \qquad \text{(slow)}$$

$$Hg + MnO_4^- \longrightarrow Hg^{++} + \text{products} \qquad \text{(fast).}$$

Of all the salts tested, $AgClO_4$ was found to have by far the greatest catalytic influence on the reaction. The effect was much greater than could be explained on the basis of the activation of $H_2$ by $Ag^+$ reported in Part I.

## Silver Ion Catalysed Reaction

To avoid complications due to heterogeneous effects such as those occurring in neutral solution (74, 75) kinetic measurements on the $Ag^+$ catalysed reaction between $MnO_4^-$ and $H_2$ were confined to acid solutions. The presence of silver salts had no effect on the stoichiometry of the reaction and no silver could be detected in the $MnO_2$ product, in contrast to neutral solutions where the product is apparently $Ag_2Mn_2O_5$ (75).

As in the uncatalysed reaction, the disappearance of $MnO_4^-$ in the presence of $AgClO_4$ was apparently first order in $MnO_4^-$, as the rate plots in Fig. 42 indicate. The plots are initially linear, but show deviations after about 50% reaction, presumably due to heterogeneous catalysis by the precipitated $MnO_2$. This is supported by the results of an experiment (see Table XVIII) in which $MnO_2$, added initially to the solution, was found to cause an increase in the rate. On the other hand, packing the

## TABLE XVIII

Kinetic data on the silver catalysed reduction of permanganate by hydrogen at 40ºC.

| Initial $KMnO_4 \times 10^3$ M. | $AgClO_4$ M. | $HClO_4$ M. | $NaClO_4$ M. | k' $l.m.^{-1}sec.^{-1}$ | k $l.m.^{-1}sec.^{-1}$ | $k_c$ $l^2.m.^{-2}sec.^{-1}$ |
|---|---|---|---|---|---|---|
| 0.5 | 0.0186 | 0.3 | - | 0.88 | 0.45 | 23 (a) |
| 0.8 | 0.0183 | 0.3 | - | 0.84 | 0.41 | 24 |
| 2.3 | 0.0184 | 0.3 | - | 0.80 | 0.40 | 22 |
| 4.0 | 0.0183 | 0.3 | - | 0.83 | 0.40 | 24 |
| 2.3 | 0.0184 | 0.3 | - | 0.85 | 0.40 | 24 (a) |
| 1.9 | 0.0184 | 0.3 | - | 1.02 | 0.48 | 29 (b) |
| 2.3 | 0.0186 | 0.3 | 0.4 | 0.76 | 0.38 | 20 |
| 2.3 | 0.0185 | 0.3 | 0.7 | 0.73 | 0.38 | 19 |
| 2.3 | 0.0186 | 0.3 | 1.0 | 0.70 | 0.37 | 18 |
| 2.3 | 0.0185 | 1.0 | - | 0.82 | 0.48 | 18 |

(a) Reaction vessel packed with Pyrex glass wool.

(b) 0.004 mole liter$^{-1}$ $MnO_2$ added initially.

Comparison of reduction rates of dichromate and of permanganate in the presence of $AgClO_4$ (at 1 atm. $H_2$)

| $AgClO_4$ M. | Temp. ºC | $-d[H_2]/dt \times 10^7$ mole $l.^{-1}sec.^{-1}$ for $Cr_2O_7^{=}$ reduction | $-d[H_2]/dt \times 10^7$ mole $l.^{-1}sec.^{-1}$ for $MnO_4^-$ reduction at $[MnO_4^-] = 10^{-3}$ M. |
|---|---|---|---|
| 0.0187 | 60 | 0.12 | 13.1 |
| 0.0559 | 40 | 0.10 | 8.7 |

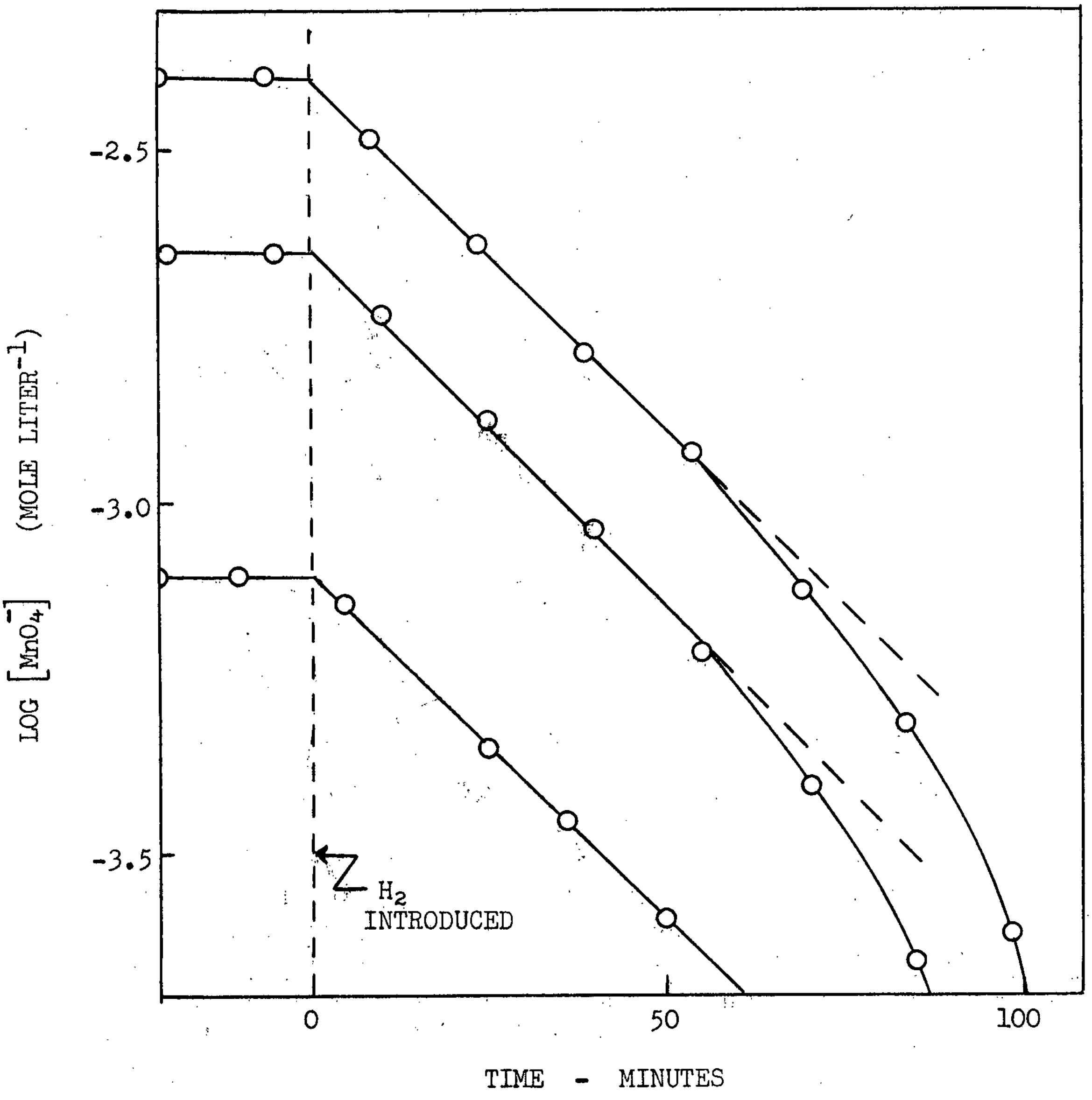


Fig. 42. Rate plots for the reduction of permanganate by hydrogen in the presence of 0.0185 M. $AgClO_4$ at 40°C. Solutions 0.3 M. $HClO_4$; $H_2$ pressure, 0.92 atm.

reaction vessel with glass wool had no effect on the rate. The initial slopes of the rate plots were found to be directly proportional to the partial pressure of hydrogen (Fig. 43) at constant $AgClO_4$ concentration.

The kinetics of the reaction, which appears to be homogeneous during the initial stages, are thus represented by,

$$-\frac{d[H_2]}{dt} = k' [H_2] [MnO_4^-] \qquad \ldots\ldots (20)$$

Values of k', estimated from initial slopes of the rate plots are reported in Table XVIII. The dependence of k' on the concentration of $Ag^+$ is depicted in Fig. 44, and is seen to be of the form,

$$k' = k + k_c[Ag^+] \qquad \ldots\ldots (21)$$

where k is the same constant as in equation (17) and $k_c$ is the third order rate constant of the silver catalysed reaction whose kinetics are of the form,

$$-\frac{d[H_2]}{dt} = k_c [H_2] [MnO_4^-] [Ag^+] \qquad \ldots\ldots (22)$$

Values of $k_c$, calculated from values of k' and of k determined from the results reported previously, are listed in Table XVIII and are seen to be essentially independent of the initial concentration of $MnO_4^-$ (between 0.0005 and 0.004 M.) and $HClO_4$ (between 0.3 and 1.0 M.). On the other hand, $k_c$ was found to decrease slightly on addition of $NaClO_4$.

Measurements of $k_c$ at different temperatures from 30° to 60°C gave the Arrhenius plot shown in Fig. 45 which is fitted by the equation,

$$k_c = 7.5 \times 10^7 \exp[(-9300 \pm 500)/RT] \ 1.^2 mole^{-2} sec.^{-1}$$

with $\Delta H^{\ddagger} = 9 \pm 0.5$ kcal. $mole^{-1}$ and $\Delta S^{\ddagger} = -25 \pm 2$ cal. $deg.^{-1} mole.^{-1}$.

The rates of reaction of $H_2$ with silver ion by the mechanism studied in Part I are small enough to be neglected in comparison to the rates of the silver catalysed reduction of permanganate (see Table XVIII).

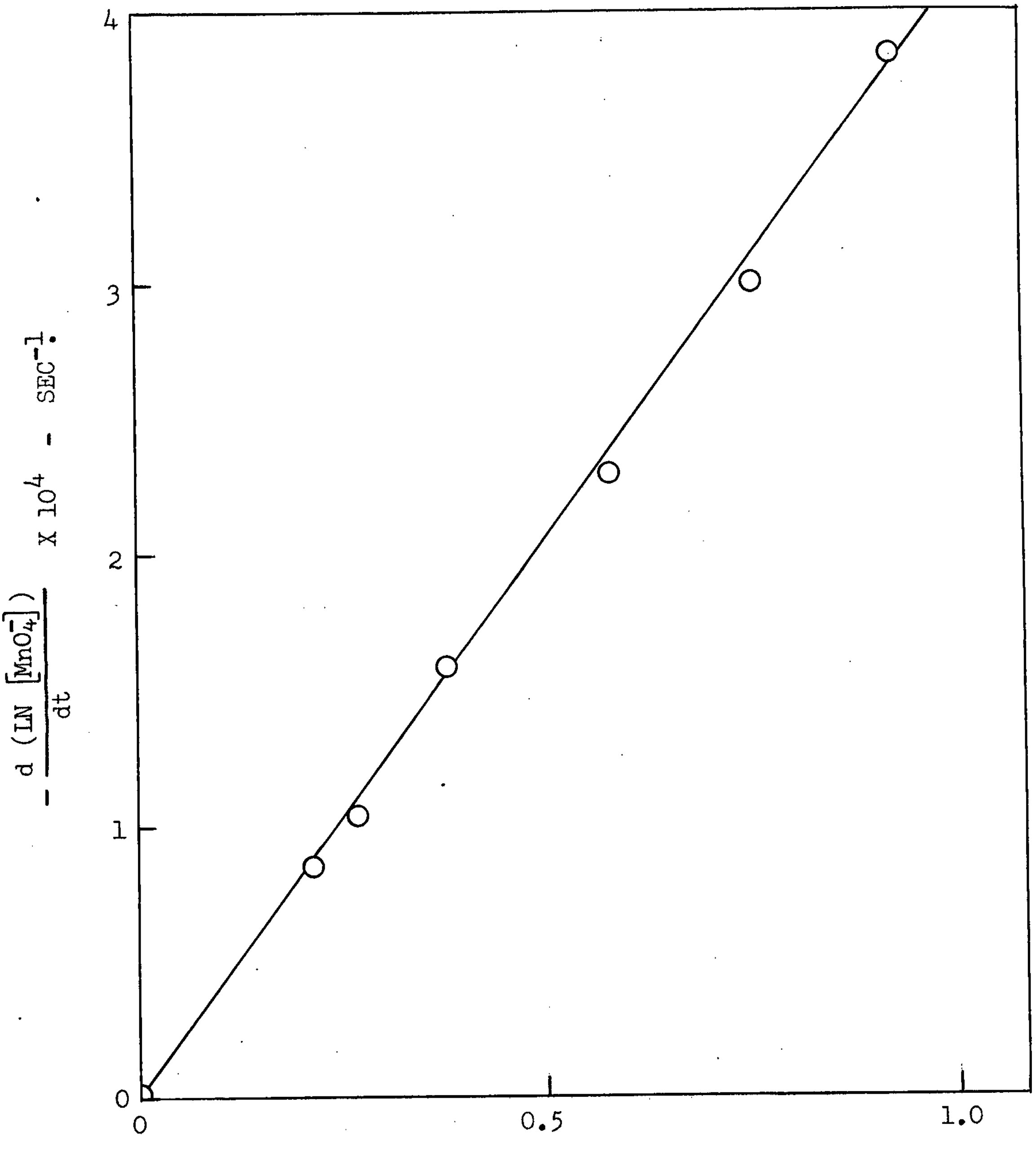


Fig. 43. Dependence of the rate of reduction of permanganate in the presence of 0.0185 M. $AgClO_4$ on hydrogen pressure. Solutions 0.3 M. $HClO_4$; Temp. 40°C.

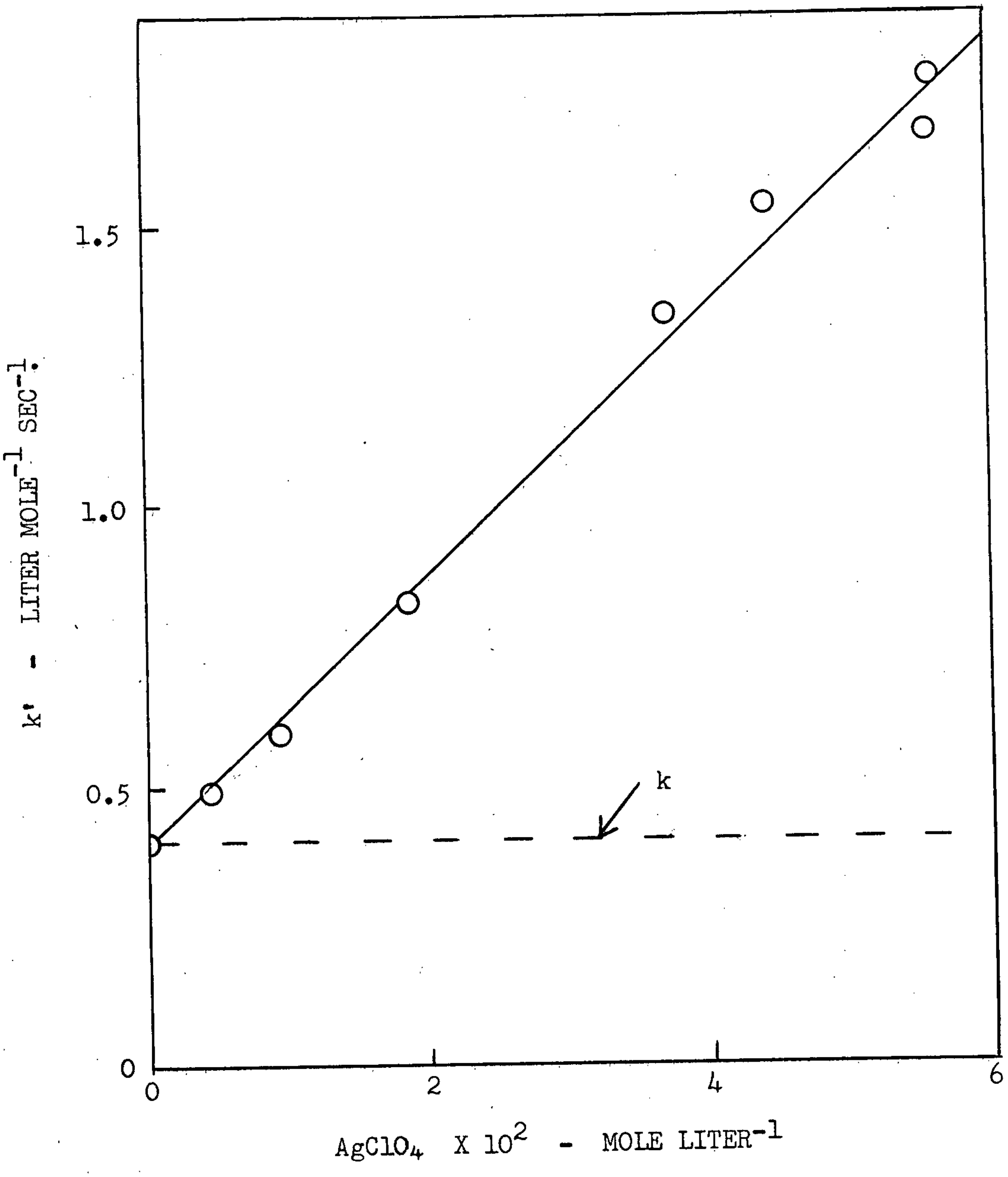


Fig. 44. Dependence of k' on the concentration of $AgClO_4$ in 0.3 M. $HClO_4$ at 40°C.

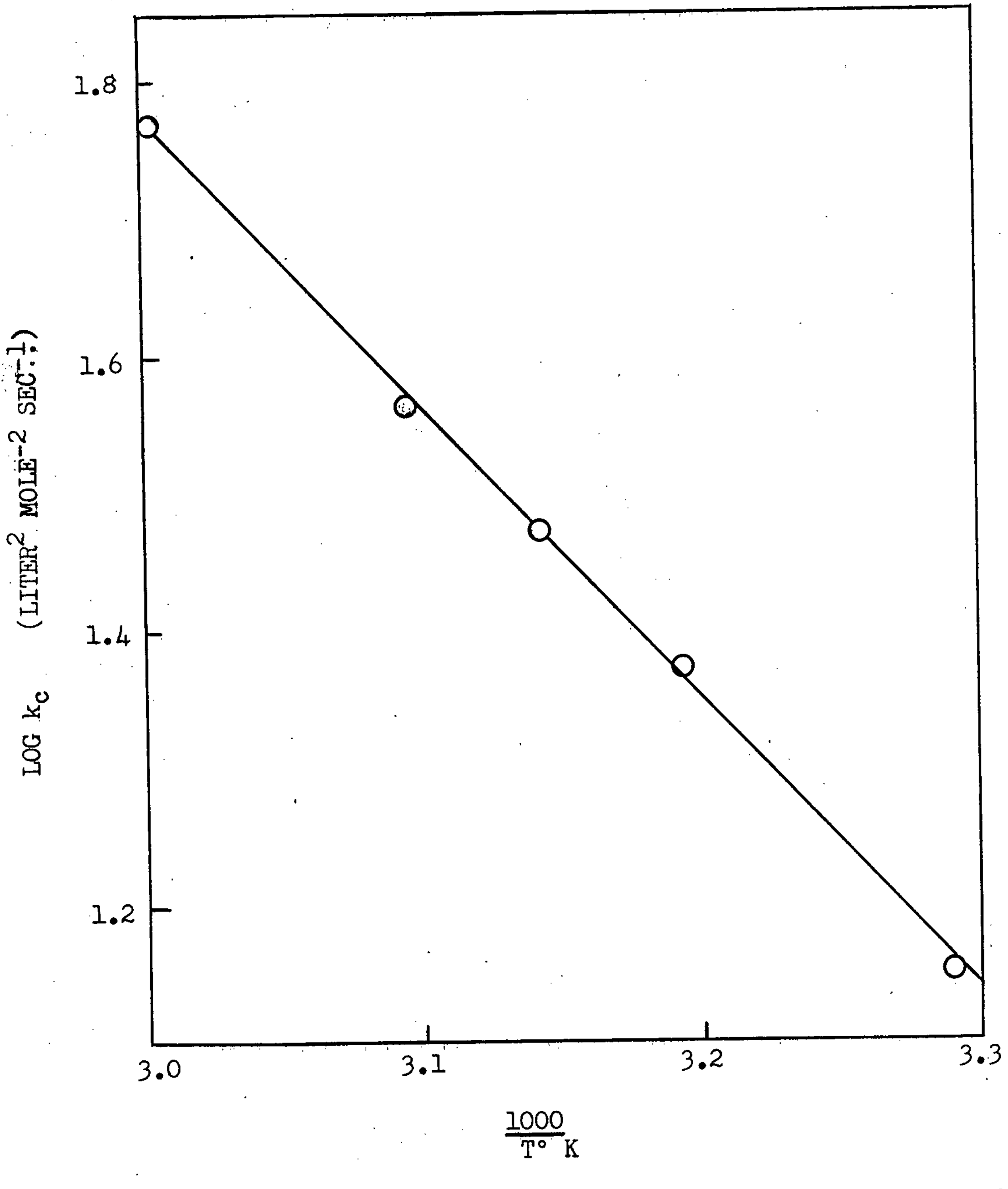


Fig. 45. Arrhenius plot for the silver catalysed reduction of permanganate in 0.3 M. $HClO_4$.

## Discussion of the Uncatalysed Reaction

The kinetics suggest that the rate determining step is a bimolecular reaction involving one $H_2$ molecule and one $MnO_4^-$ ion giving an intermediate Mn species which undergoes further rapid reactions to yield the stable products, $MnO_2$ in acid and neutral solutions and $MnO_4^=$ in basic solution. The absence of an appreciable salt effect is normal for a reaction between an ion and an uncharged molecule. The increase in rate with increasing acidity may reflect the formation of some undissociated $HMnO_4$ which is more reactive than $MnO_4^-$.

The absence of an induction period and fluoride retardation support the view that the reaction does not proceed through a Mn(III) intermediate. Such an intermediate has been suggested for the oxidation of oxalic acid (95, 96) and certain other reactions (97, 98). The fluoride inhibition in these processes has been attributed to the formation of an Mn(III) - $F^-$ complex.

Possible intermediates are Mn(VI) and Mn(V) both of which would be expected to react rapidly under the experimental conditions to give the observed products. Of the two possibilities, the latter is considered more likely since the formation of Mn(VI) by reaction between $MnO_4^-$ and $H_2$, i.e.,

$$MnO_4^- + H_2 \longrightarrow MnO_4^= + H + H^+ \qquad \text{......} \ (23)$$

is accompanied by the formation of an H atom and is endothermic by about 21 kcal. $mole^{-1}$ (83, 89). In the absence of a $OH^-$ concentration dependence, the step,

$$MnO_4^- + OH^- \longrightarrow MnO_4^= + \cdot OH$$

which has been proposed for certain permanganate reactions (100) would appear unlikely. On the other hand, the formation of Mn(V) through one of the following reactions seems plausible,

$$MnO_4^- + H_2 \longrightarrow MnO_4^{=} + 2\ H^+ \qquad \ldots\ldots\ (24)$$

$$MnO_4^- + H_2 \longrightarrow MnO_3^- + H_2O \qquad \ldots\ldots\ (25)$$

The process represented by equation (24) is exothermic by about 56 kcal. mole$^{-1}$ (99). The suggestion that the reaction between $MnO_4^-$ and $H_2$ proceeds through the intermediate formation of Mn(V) was originally made by Just and Kauko (63). The existence of Mn(V) in solution is well established (94) and this species has also been postulated as an intermediate in the reaction of $MnO_4^-$ with certain organic compounds (101, 102, 103, 104). The rather low frequency factor of the reaction, corresponding to an apparent activation entropy of -17 cal. deg.$^{-1}$mole$^{-1}$, might find an explanation on the basis of the mechanism represented by equation (24) since the activated complex in this case would probably be more ionic, and hence more highly hydrated, than the reactants.

## Discussion of the Silver Catalysed Reaction

From an examination of equation (23), it would appear possible that the formation of Mn(VI) would be favoured by the presence of another species which readily accepts an electron or combines with an H atom. The catalytic activity of $Ag^+$ in this reaction may be due to its fulfilling this role, and the rate determing step of the catalysed reaction may be,

$$Ag^+ + MnO_4^- + H_2 \longrightarrow AgH^+ + MnO_4^{=} + H^+ \qquad \ldots\ldots\ (26)$$

or alternatively,

$$AgMnO_4 + H_2 \longrightarrow AgH^+ + MnO_4^- + H^+ \qquad \ldots\ldots\ (27)$$

preceeded by the equilibrium,

$$Ag^+ + MnO_4^- \rightleftharpoons AgMnO_4 \qquad \ldots\ldots\ (28)$$

In either case the rate determining step would be followed by rapid reactions of $MnO_4^{=}$ and of $AgH^+$ to give the observed products. Both possibilities are consistent with the third order kinetics and, providing that the equilibrium concentration of $AgMnO_4$ is small, they are not readily distinguishable.

Results of spectrophotometric measurements made at 270 m$\mu$ are summarized in Fig. 46. $(D_{total} - D_{Ag^+}) / MnO_4^-$ is plotted against silver ion concentration for solutions in which $[Ag^+] >> [MnO_4^-]$. Although the scatter is large, an enhancement of the $MnO_4^-$ absorption is apparent, providing some evidence for the formation of undissociated $AgMnO_4$. The formation of this species was also suggested by Hein (75) to account, in part, for the silver catalysed hydrogenation of permanganate in neutral solution.

The slight negative salt effect is consistent with a mechanism involving two ions of opposite charge.

The species $AgH^+$ has been suggested in Part I as an intermediate in mechanism (I) for the $Ag^+$ catalysed reaction between $H_2$ and $Cr_2O_7^=$. There is a resemblance between this mechanism, involving the activation of hydrogen by interaction with two silver ions, and the $Ag^+$ catalysed hydrogenation of $MnO_4^-$. In the latter system, $MnO_4^-$ effectively replaces one of the $Ag^+$ ions as an acceptor for an H atom (or an electron). This reaction path is favoured because of its low activation energy (ca. 9 kcal. mole$^{-1}$), presumably reflecting the high electron affinity of $MnO_4^-$.

Alternative mechanisms might involve pre-equilibria giving bi- or trivalent silver ions which would react with $H_2$, i.e.,

$$Ag^+ + MnO_4^- \longrightarrow Ag^{++} + MnO_4^= \qquad ......(29)$$

$$Ag^+ + MnO_4^- \longrightarrow Ag^{+++} + MnO_4^{\equiv} \qquad ......(30)$$

$$Ag^+ + MnO_4^- \longrightarrow AgO^+ + MnO_3^- \qquad ......(31)$$

However, $\Delta F^0$ for process (29) is about +32 kcal. mole$^{-1}$ (105) while $\Delta F^{\ddagger}$ of activation for the reaction studied is only +17 kcal. mole$^{-1}$. The

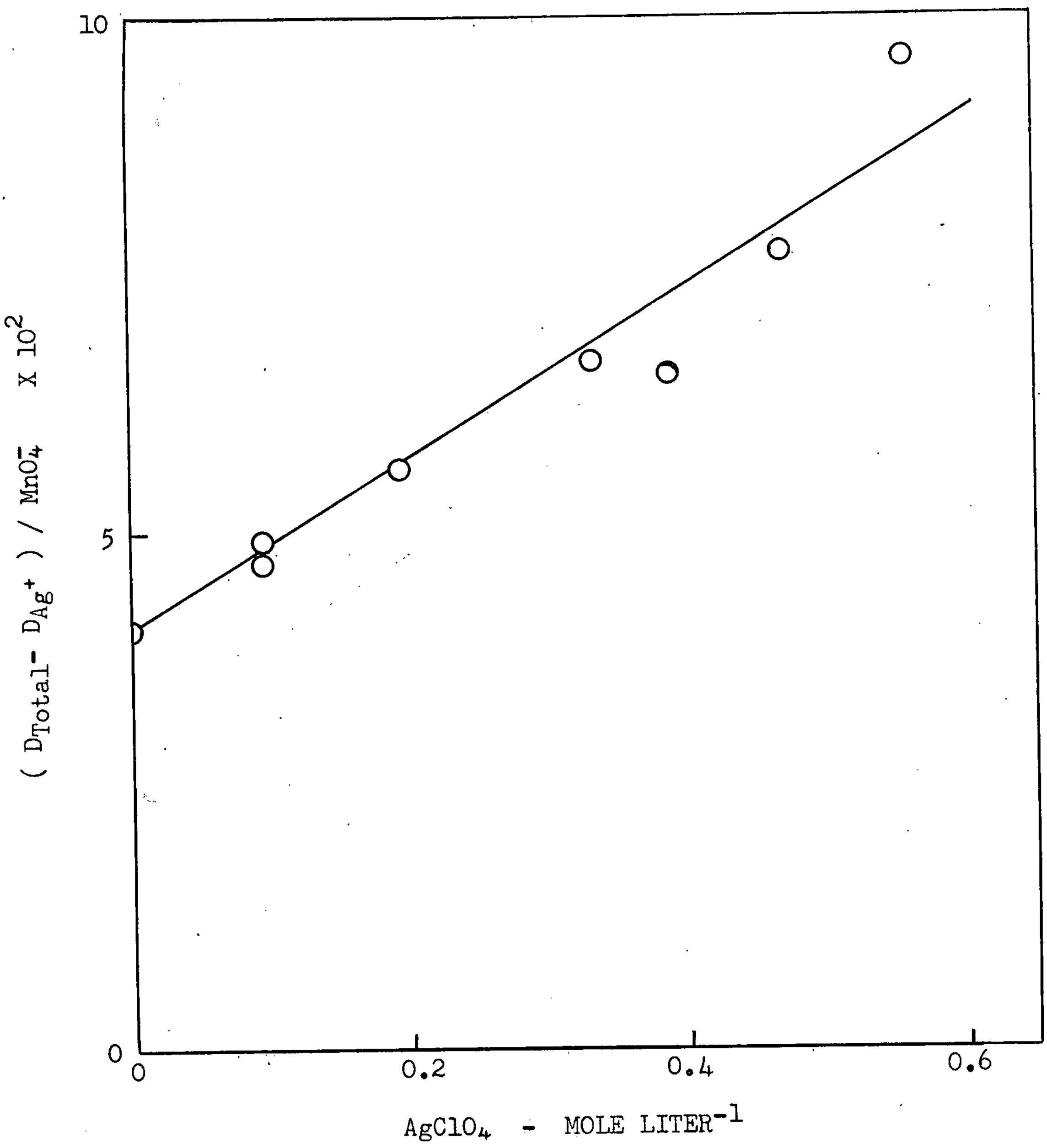


Fig. 46. Variation of $MnO_4^-$ absorption at 270 mμ with silver ion concentration.

equilibria involving trivalent silver would probably be even more unfavourable. It is believed that either $Ag^{+++}$ (106, 107) or $Ag^{++}$ (108) is an intermediate in the silver ion catalysed $S_2O_8^{=}$ oxidations; in these reactions, however, the rate is found to be essentially independent of the concentration of the reducing agent (106, 107). It would appear, therefore, that such a mechanism is unlikely in the present instance.

## GENERAL DISCUSSION

It would appear that hydrogen can react in the presence of silver ion by at least three different mechanisms: reactions which involve in the initial step (a) two silver ions and one hydrogen molecule, (b) one silver ion and one hydrogen molecule, and (c) a silver ion acting in combination with a specific oxidizing agent ($MnO_4^-$) as a specific catalyst for reduction of the latter.

The first type of reaction, giving third order kinetics, is similar to the activation of hydrogen by CuOAc in quinoline. An activated complex of the form $Ag_2H_2^{++}$ is indicated; this may decompose to intermediates such as 2 $AgH^+$. Since no proton is released in this process, the absence of large acid or base effects on the kinetics appears reasonable.

The second type of reaction resembles the activation of hydrogen by $Cu^{++}$ and the reduction of AgOAc in pyridine. The initial step probably involves the formation of a hydride intermediate, AgH, and the release of a proton. Stabilization of this proton by a base increases the rate of reaction and prevents back reactions; the relative rates of reaction of the complexes are indicated in Table XIX.

The first two types of reaction are represented schematically by the potential energy diagrams shown in Fig. 47; uncertainties in the energies of intermediates precludes any attempt to make the representation quantitative.

These two reactions may, perhaps, be differentiated on the basis of the mechanism whereby the molecular hydrogen becomes activated, i.e., homolytic fission in which the hydrogen splits symmetrically forming 2 $AgH^+$,

# TABLE XIX

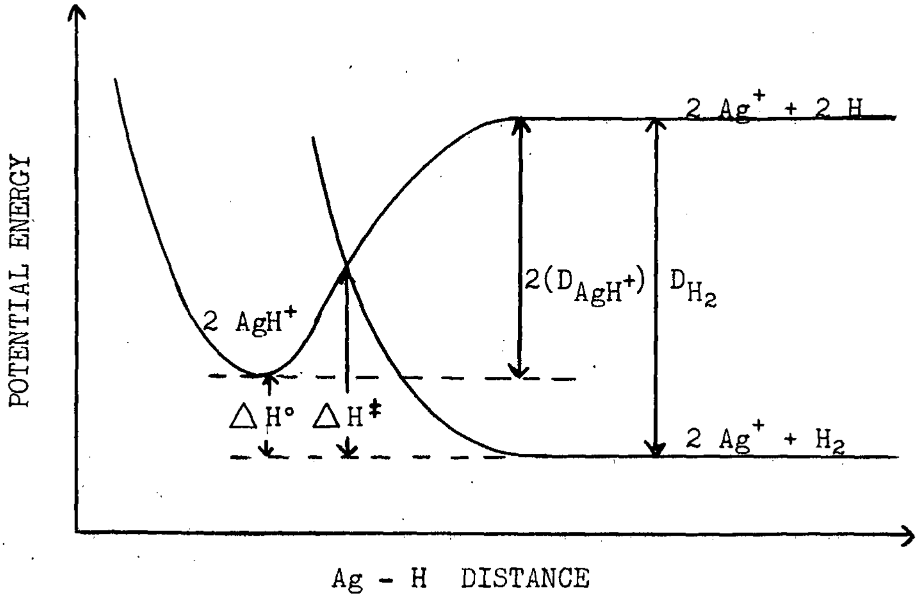
Relative reactivities of complexes of Ag(I)

| Complexing Agent | $pK_A$ |  | Rate of activation of $H_2$ relative to hydrated ion | N No. of ligands per complex | $\frac{1}{N} \log K_{st}$ |
|---|---|---|---|---|---|
|  | 1 | 2 |  |  |  |
| Ethylene diamine | 7.2 | 10.0 | 25 ± 3 * | 2 | 3.9 |
| Cyanide | 9.4 | - | <0.5 | 2 | 9.2 |
| Acetate | 4.76 | - | 80 ± 20 * | 1 | 0.73 |
| Water | - | - | 1 | - | - |

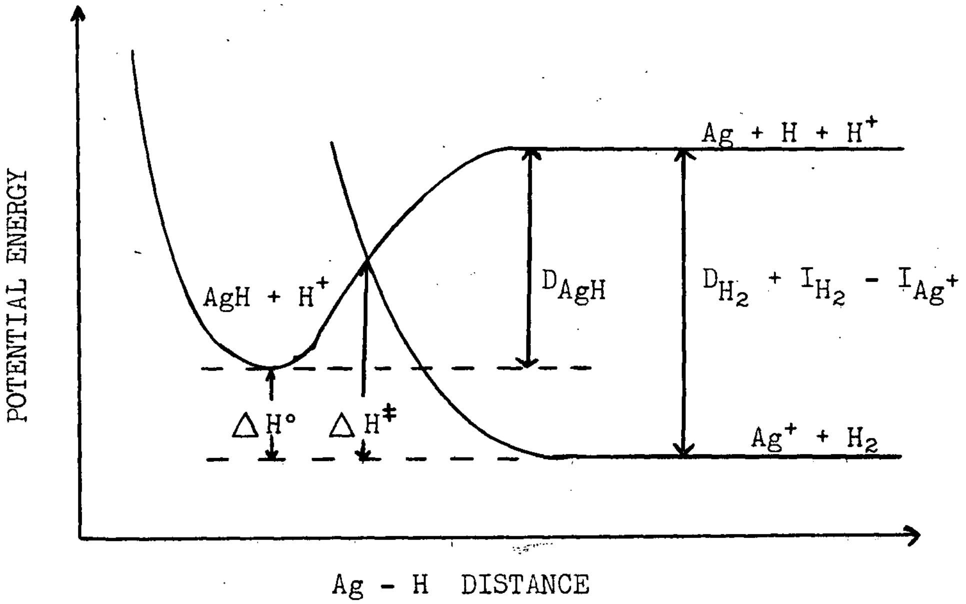
* k at 70°C divided by $k_{II}$ calculated for 70°C.

$$pK_A = -\log \frac{[B]\,[H^+]}{[BH^+]} \qquad K_{st} = \frac{[MB_n]}{[M]\,[B]^n}$$

References: (69), (70), (91), (93), (105).


POTENTIAL ENERGY
2 Ag$^+$ + 2 H
2 AgH$^+$
2(D$_{AgH^+}$)
D$_{H_2}$
ΔH°
ΔH‡
2 Ag$^+$ + H$_2$
Ag - H DISTANCE

Mechanism I - Homolytic Fission.


POTENTIAL ENERGY
Ag + H + H$^+$
AgH + H$^+$
D$_{AgH}$
D$_{H_2}$ + I$_{H_2}$ - I$_{Ag^+}$
ΔH°
ΔH‡
Ag$^+$ + H$_2$
Ag - H DISTANCE

Mechanism II - Heterolytic Fission.

Fig. 47. Potential energy curves for the reactions between silver ion and molecular hydrogen - all processes refer to aqueous solution.
(Qualitative only)

and heterolytic fission in which the hydrogen splits asymmetrically forming AgH and $H^+$. It has been suggested (36) that such a classification may apply to other hydrogenation reactions, e.g. homolytic fission of $H_2$ in reaction with $Hg_2^{++}$, and heterolytic fission of $H_2$ in reaction with $Cu^{++}$ in aqueous solution. In the Ag(I) system activation by both mechanisms appears to take place simultaneously.

The third type of reaction is illustrated by the silver catalysed reduction of permanganate. The initial step may involve the acceptance of an electron by the permanganate and the acceptance of a hydrogen atom by the silver ion. A mechanism similar to this may account for the catalytic effect of silver salts on the permanganate oxidation of organic compounds such as acetone, methanol, and stilbene (75).

In the reduction of silver perchlorate in the absence of a reducible substrate, the nucleation apparently involves a process of high order in $Ag^+$. The presence of a base probably results in faster nucleation, reflected in a smaller particle size (Fig. 49).

A comparison of the reduction rates of the oxy-anions $MnO_4^-$, $CrO_4^=$, and $ClO_4^-$ is of interest. The first is reduced by hydrogen directly, the second is reduced only in the presence of a catalyst, the third is not reduced at all under the conditions used in these experiments. In permanganate there are vacant 3d orbitals which should be capable of accepting electrons from the hydrogen. In chromate, iso-electronic with permanganate, the energies of these orbitals will be higher on account of the lower nuclear charge on chromium. This results in the relative instability of Cr(V) and Cr(IV) oxy-anions which might be expected as intermediates. Perchlorate, the reduction of which is also favourable thermodynamically, possesses no low energy unoccupied orbitals; the first unoccupied level is the 4s, which has a considerably higher energy than the bonding orbitals.

# REFERENCES

1. Forward, F.A., Trans.Can.Inst.Mining Met., 56, 363 (1953).

2. Schaufelberger, F.A., A.I.M.E.Trans., 206, 695 (1956).

3. Halpern, J., A.I.M.E.Trans., 209, 280 (1957).

4. Macgregor, E.R., M.A.Sc. Thesis, University of British Columbia (1956).

5. Schaufelberger, F.A., and T.K. Roy, Trans.Inst.Mining and Metallurgy (London), 64, 375 (1954-55).

6. Forward, F.A., and J. Halpern, Trans.Can.Inst.Mining Met., 56, 355 (1953).

7. O'Brien, R.N., F.A. Forward, and J. Halpern, Trans.Can.Inst. Mining Met., 56, 359 (1953).

8. Korinek, G.J., Ph.D. Thesis, University of British Columbia (1956).

9. Baker, M.M., and G.I. Jenkins, Advances in Catalysis, 7, 1 (1955).

10. Dowden, D.A., and P.W. Reynolds, Nature, 164, 50 (1949).

11. Dowden, D.A., J.Chem.Soc., 242 (1950).

12. Selwood, P.W., J.Am.Chem.Soc., 78, 249 (1956).

13. Couper, A., and D.D. Eley, Disc.Farad.Soc., 8, 172 (1950).

14. Dowden, D.A., and P.W. Reynolds, Disc.Farad.Soc., 8, 185 (1950).

15. Maxted, E.B., J.Chem.Soc., 1987 (1949).

16. Maxted, E.B., and K.L. Moon, J.Chem.Soc., 2171 (1949).

17. Beeck, O., Disc.Farad.Soc., 8, 118 (1950).

18. Bodenstein, M., and S.C. Lind, Zeit für physik.Chem., 57, 168 (1907).

19. Herzfeld, K.F., Ann.Physik., 59, 635 (1919).

20. Wheeler, A., and R.N. Pease, J.Am.Chem.Soc., 58, 1665 (1936).

21. Rice, F.O., and K.F. Herzfeld, J.Am.Chem.Soc., 56, 284 (1934).

22. Varnerin, R.E., and J.S. Dooling, J.Am.Chem.Soc., 78, 1119 (1956).

23. Smith, M.J., P.M. Beatty, J.A. Pinder, and D.J. LeRoy, Can.J.Chem., 33, 821 (1955).

24. Bodenstein, M., Zeit.für physik.Chem., 29, 295 (1899).

25. Beeck, O., Rev.Mod.Phys., 17, 61 (1945).

26. Parravano, G., and M. Boudart, Advances in Catalysis, 7, 47 (1955).

27. Molinari, E., and G. Parravano, J.Am.Chem.Soc., 75, 5233 (1953).

28. Voltz, S.E., and S. Weller, J.Am.Chem.Soc., 75, 5227 (1953).

29. Voltz, S.E., and S. Weller, J.Phys.Chem., 59, 569 (1955).

30. Heckelsberg, L.F., G.C. Bailey, and A. Clark, J.Am.Chem.Soc., 77, 1373 (1955).

31. Pease, R.N., and H.S. Taylor, J.Am.Chem.Soc., 43, 2179 (1921).

32. Parravano, G., J.Am.Chem.Soc., 74, 1194 (1952).

33. van Tiggelen, A., L. Vanreusel, and P. Neven, Bull.soc.chim.Belges, 61, 651 (1952); C.A. 7402 (1954).

34. Farkas, L., and E. Fischer, J.Biol.Chem., 167, 787 (1947).

35. Krasna, A.I., and D. Rittenberg, J.Am.Chem.Soc., 76, 3015 (1954).

36. Halpern, J., Quart.Rev., 10, 463 (1956).

37. Weller, S., and G.A. Mills, Advances in Catalysis, 8, 163 (1956).

38. Wright, L.W., S. Weller, and G.A. Mills, J.Phys.Chem. 59, 1060 (1955).

39. Wilmarth, W.K., and A.F. Kapauan, J.Am.Chem.Soc., 78, 1308 (1956).

40. Calvin, M., Trans.Farad.Soc., 34, 1181 (1938).

41. Calvin, M., J.Am.Chem.Soc., 61, 2230 (1939).

42. Weller, S., and G.A. Mills, J.Am.Chem.Soc., 75, 769 (1953).

43. Calvin, M., and W.K. Wilmarth, J.Am.Chem.Soc., 78, 1301 (1956).

44. Wilmarth, W.K., and M.K. Barsh, J.Am.Chem.Soc., 78, 1305 (1956).

45. Wilmarth, W.K., M.K. Barsh, and S.S. Dharmatti, J.Am.Chem.Soc., 74, 5035 (1952).

46. Wilmarth, W.K., and M.K. Barsh, J.Am.Chem.Soc., 75, 2237 (1953).

47. Flynn, J.H., and H.M. Hulbert, J.Am.Chem.Soc., 76, 3393 (1954).

48. Adkins, H., and G. Krsek, J.Am.Chem.Soc., 71, 3051 (1949).

49. Natta, G., R. Ercoli, S. Castellano, and F.H. Barbieri, J.Am.Chem.Soc., 76, 4049 (1954).

50. Martin, A.R., Chemistry and Industry, 1536 (1954).

51. Wender, I., S. Metlin, S. Ergun, H.W. Sternberg, and H. Greenfield, J.Am.Chem.Soc., 78, 5401 (1956).

52. Wilmarth, W.K., and J.C. Dayton, J.Am.Chem.Soc., 75, 4553 (1953).

53. Halpern, J., and E. Peters, J.Chem.Phys., 23, 605 (1955).

54. Peters, E., and J. Halpern, J.Phys.Chem., 59, 793 (1955).

55. Halpern, J., E.R. Macgregor, and E. Peters, J.Phys.Chem., 60, 1455 (1956).

56. Peters, E., and J. Halpern, Can.J.Chem., 33, 356 (1955).

57. Peters, E., and J. Halpern, Can.J.Chem., 34, 554 (1956).

58. Dakers, R.G., and J. Halpern, Can.J.Chem., 32, 969 (1954).

59. Halpern, J., and R.G. Dakers, J.Chem.Phys., 22, 1272 (1954).

60. Korinek, G.J., and J. Halpern, J.Phys.Chem., 60, 285 (1956).

61. Korinek, G.J., and J. Halpern, Can.J.Chem., 34, 1372 (1956).

62. Halpern, J., G.J. Korinek, and E. Peters, Research (London), 7, S61 (1954).

63. Just, G., and Y. Kauko, Zeit.für physik.Chem., 76, 60 (1911).

64. Wilke, E., and H. Kuhn, Zeit.für physik.Chem., 113, 313 (1924).

65. Delwaulle, M.L., Comptes rendus, 192, 1736 (1931).

66. Wilmarth, W.K., J.C. Dayton, and J.M. Flourney, J.Am.Chem.Soc., 75, 4549 (1953).

67. Wright, L.W., and S. Weller, J.Am.Chem.Soc., 76, 3345 (1954).

68. Kaneko, T.M., and M.E. Wadsworth, J.Phys.Chem., 60, 457 (1956).

69. Harned, H.S., and B.B. Owen, Chem.Rev., 25, 31 (1939).

70. Martell, E.A., and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall Inc., New York, N.Y., 1952, pp. 518, 528.

71. Bjerrum, J., Chem.Rev., 46, 381 (1950).

72. Beketoff, M.N., Comptes rendus, 48, 442 (1859).

73. Knacke, O., F. Pawlek, and E. Süssmuth, Zeit.für Erzbergbau und Metallhüttenwesen, 9, 566 (1956).

74. Hein, F., and W. Daniel, Zeit.für anorg.Chem., 181, 78 (1929).

75. Hein, F., W. Daniel, and H. Schwedler, Zeit.für anorg.Chem., 233, 161 (1937).

76. Sircar, S.C., S. Aditya, and B. Prasad, J.Indian Chem.Soc., 30, 633 (1953), C.A., 48, 5611 (1954).

77. Kirshenbaum, I., "The Physical Properties and Analysis of Heavy Water", McGraw Hill Book Company Inc., 1951, pp. 17, 54.

78. Westheimer, F.H., Chem.Rev., 45, 419 (1949).

79. Pray, H.A., C.E. Schweickert, and B.H. Minnich, Ind.Eng.Chem., 44, 1146 (1952).

80. Wiebe, R., and V.L. Gaddy, J.Am.Chem.Soc., 56, 76 (1934).

81. Tong, J.Y., and E.L. King, J.Am.Chem.Soc., 75, 6180 (1953).

82. Rollefson, G.K., J.Phys.Chem., 56, 976 (1953).

83. Rossini, F.D., et al., "Selected Values of Chemical Thermodynamic Properties." U.S. Bureau of Standards, circular 500 (1952).

84. Farkas, A., Zeit.für physik.Chem., B5, 467 (1929).

85. Courtney, W.G., J.Phys.Chem., 60, 1461 (1956).

86. Waters, D.N., and L.A. Woodward, J.Chem.Soc., 3250 (1954).

87. Bell, R.P., Advances in Catalysis, 4, 151 (1952).

88. Kleman, B., and S. Lindkvist, Arkiv.Fys., 9, 385 (1955).

89. Conway, B.E., "Electrochemical Data", Elsevier Publishing Company, New York, N.Y., 1952, pp. 75-83.

90. Abel, E., E. Bratu, and O. Redlich, Zeit.für physik.Chem., 173, 353 (1935).

91. MacDougall, F.H., and L.F. Topol, J.Phys.Chem., 56, 1090 (1952).

92. Schwarzenbach, G., H.A. Ackermann, B. Maissen, and G. Anderegg, Helv.Chim. Acta, 35, 2337 (1952).

93. Pearson, R.G., and F. Basolo, J.Am.Chem.Soc., 78, 4876 (1956).

94. Pode, J.S.F., and W.A. Waters, J.Chem.Soc., 717 (1956).

95. Launer, H.F., and D.M. Yost, J.Am.Chem.Soc., 56, 2571 (1934).

96. Adler, S.J., and R.M. Noyes, J.Am.Chem.Soc., 77, 2037 (1955).

97. Tompkins, F.C., Trans.Farad.Soc., 38, 131 (1942).

98. Alexander, E.A., and F.C. Tompkins, Trans.Farad.Soc., 35, 1156 (1939).

99. Carrington, A., and M.C.R. Symons, J.Chem.Soc., 3373 (1956).

100. Symons, M.C.R., J.Chem.Soc., 3956 (1954).

101. Mann, D.R., and F.C. Tompkins, Trans.Farad.Soc., 37, 201 (1941).

102. Tompkins, F.C., Trans.Farad.Soc., 39, 28 (1943).

103. Wiberg, K.B., and R. Stewart, J.Am.Chem.Soc., 77, 1786 (1955).

104. Wiberg, K.B., and R. Stewart, J.Am.Chem.Soc., 78, 1214 (1956).

105. Latimer, W.M., "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", Prentice-Hall Inc., N.Y., 1938.

106. Yost, D.M., J.Am.Chem.Soc., 48, 152 (1926).

107. Dekker, A.O., H.A. Levy, and D.M. Yost, J.Am.Chem.Soc., 59, 2129 (1937).

108. Bawn, C.E.H., and D. Margerison, Trans.Farad.Soc., 51, 925 (1955).

# APPENDIX A

## SUMMARY OF EXPERIMENTAL RESULTS

## SILVER ION CATALYSED REDUCTION OF DICHROMATE BY HYDROGEN

(a) Effect of partial pressure of hydrogen.

Temp. 49.6°C; 0.5 M. $HClO_4$; 0.1 M. $AgClO_4$

| $P_{H_2}$ atm. | $-\frac{d[H_2]}{dt} \times 10^8$ $m.l.^{-1}sec.^{-1}$ | $-\left.\frac{d[H_2]}{dt}\right]_I \times 10^8$ $m.l.^{-1}sec.^{-1}$ | $k_I \times 10^3$ $l.^2m.^{-2}sec.^{-1}$ |
|---|---|---|---|
| 0 | (0.07) | - | - |
| 0.23 | 1.42 | 1.23 | 7.5 |
| 0.34 | 2.16 | 1.88 | 7.7 |
| 0.47 | 2.85 | 2.49 | 7.2 |
| 0.63 | 3.81 | 3.29 | 7.2 |
| 0.87 | 5.30 | 4.58 | 7.3 |

(b) Effect of variation of silver perchlorate concentration.

Temp. 50.0°C; 0.5 M. $HClO_4$

| $AgClO_4$ M. | $P_{H_2}$ atm. | $-\frac{d[H_2]}{dt} \times 10^8$ $m.l.^{-1}sec.^{-1}$ | $-\left.\frac{d[H_2]}{dt}\right]_I \times 10^8$ (at $P_{H_2}$ = 1 atm.) $m.l.^{-1}sec.^{-1}$ | $k_I \times 10^3$ $l.^2m.^{-2}sec.^{-1}$ |
|---|---|---|---|---|
| 0.0395 | 0.88 | 1.03 | 0.87 | 7.7 |
| 0.0600 | 0.87 | 2.08 | 1.89 | 7.2 |
| 0.0776 | 0.87 | 3.44 | 3.29 | 7.5 |
| 0.1002 | 0.88 | 5.24 | 5.11 | 7.0 |
| 0.1087 | 0.88 | 6.20 | 6.13 | 7.2 |

(c) Effect of variation of silver perchlorate concentration.

Temp. 40.0°C; 0.5 M. $HClO_4$

| $AgClO_4$ | $P_{H_2}$ | $-\frac{d[H_2]}{dt} \times 10^8$ | $-\left.\frac{d[H_2]}{dt}\right]_I \times 10^8$ (at $P_{H_2} = 1$ atm.) | $k_I \times 10^3$ |
|---|---|---|---|---|
| M. | atm. | $\text{m.l.}^{-1}\text{sec.}^{-1}$ | $\text{m.l.}^{-1}\text{sec.}^{-1}$ | $\text{l.}^{2}\text{m.}^{-2}\text{sec.}^{-1}$ |
| 0.0397 | 0.93 | 0.51 | 0.45 | 3.6 |
| 0.0602 | 0.93 | 1.07 | 0.99 | 3.7 |
| 0.0803 | 0.94 | 1.80 | 1.69 | 3.5 |
| 0.1002 | 0.90 | 2.52 | 2.54 | 3.4 |
| 0.1082 | 0.93 | 3.00 | 2.95 | 3.4 |

(d) Effect of variation of silver perchlorate concentration.

Temp. 70.0°C; 0.5 M. $HClO_4$

| $AgClO_4$ | $P_{H_2}$ | $-\frac{d[H_2]}{dt} \times 10^8$ | $-\left.\frac{d[H_2]}{dt}\right]_I \times 10^8$ (at $P_{H_2} = 1$ atm.) | $k_I \times 10^3$ |
|---|---|---|---|---|
| M. | atm. | $\text{m.l.}^{-1}\text{sec.}^{-1}$ | $\text{m.l.}^{-1}\text{sec.}^{-1}$ | $\text{l.}^{2}\text{m.}^{-2}\text{sec.}^{-1}$ |
| 0.0198 | 0.69 | 1.02 | 0.87 | 31 |
| 0.0402 | 0.71 | 3.6 | 3.4 | 29 |
| 0.0604 | 0.71 | 7.5 | 7.5 | 29 |
| 0.0796 | 0.69 | 12.1 | 12.7 | 28 |
| 0.1001 | 0.69 | 17.7 | 19.8 | 27 |
| 0.1005 | 0.70 | 17.9 | 19.8 | 27 |

(e) Effect of variation of silver nitrate concentration.

Temp. 50.0°C; 0.5 M. $HNO_3$

| $AgNO_3$ M. | $P_{H_2}$ atm. | $-\frac{d[H_2]}{dt} \times 10^8$ m.l.$^{-1}$sec.$^{-1}$ | $-\frac{d[H_2]}{dt} \times 10^8$ (at $P_{H_2}$ = 1 atm.) m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|---|
| 0.0399 | 0.88 | 0.92 | 1.04 |
| 0.0600 | 0.88 | 1.89 | 2.14 |
| 0.0798 | 0.88 | 3.24 | 3.69 |
| 0.1001 | 0.88 | 4.80 | 5.45 |
| 0.1079 | 0.88 | 5.52 | 6.26 |

(f) Effect of temperature.

0.100 M. $AgClO_4$

| Temp. °C | $P_{H_2}$ atm. | $-\frac{d[H_2]}{dt} \times 10^8$ m.l.$^{-1}$sec.$^{-1}$ | $-\left.\frac{d[H_2]}{dt}\right]_I \times 10^8$ m.l.$^{-1}$sec.$^{-1}$ | $k_I \times 10^3$ l.$^2$m.$^{-2}$sec.$^{-1}$ |
|---|---|---|---|---|
| 30.0 | 0.95 | 1.22 | 1.14 | 1.57 |
| 49.6 | 0.88 | 5.29 | 4.54 | 7.1 |
| 60.0 | 0.80 | 9.94 | 8.00 | 14.2 |

(g) Effect of partial pressure of hydrogen.

Temp. 110.0°C; 0.03 M. $HClO_4$

| $Cr_2O_7^= \times 10^3$ Initial M. | $P_{H_2}$ atm. | $AgClO_4 \times 10^3$ M. | $-\frac{d[H_2]}{dt} \times 10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|---|
| 1.67 | 1.0 | 9.6 | 1.4 |
| 1.67 | 2.0 | 9.5 | 2.9 |
| 1.67 | 3.0 | 9.5 | 4.4 |
| 2.50 | 4.0 | 9.6 | 6.5 |

(h) Effect of variation of silver perchlorate concentration.

Temp. 110.0°C; $H_2$ pressure 4.0 atm.; 0.03 M. $HClO_4$

2.5 X $10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $AgClO_4$ X $10^3$ M. | $-\frac{d[H_2]}{dt}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\frac{d[H_2]}{dt}\Big]_{II}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 2.48 | 0.54 | 0.49 |
| 5.02 | 2.23 | 2.01 |
| 7.58 | 4.55 | 4.05 |
| 9.52 | 6.5 | 5.7 |
| 12.49 | 10.0 | 8.7 |
| 14.68 | 12.9 | 11.0 |

(i) Effect of variation of silver perchlorate concentration.

Temp. 110.0°C; $H_2$ pressure 4.0 atm.; 0.102 M. $HClO_4$

2.5 X $10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $AgClO_4$ X $10^3$ M. | $-\frac{d[H_2]}{dt}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\frac{d[H_2]}{dt}\Big]_{II}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 7.51 | 1.97 | 1.48 |
| 9.95 | 3.50 | 2.63 |
| 12.48 | 5.35 | 3.99 |
| 15.13 | 7.6 | 5.6 |
| 17.63 | 10.0 | 7.3 |

(j) Effect of variation of perchloric acid concentration.

Temp. 110.0°C; $H_2$ pressure 4.0 atm.; $9.5 \times 10^{-3}$ M. $AgClO_4$

$2.5 \times 10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $HClO_4$ M. | $NaClO_4$ M. | $-\frac{d[H_2]}{dt} \times 10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\left.\frac{d[H_2]}{dt}\right]_{II} \times 10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|---|
| 0.0199 | 0.28 | 6.9 | 6.1 |
| 0.0301 | 0.27 | 5.8 | 5.0 |
| 0.0522 | 0.25 | 4.6 | 3.8 |
| 0.0770 | 0.22 | 3.5 | 2.7 |
| 0.1041 | 0.20 | 3.0 | 2.2 |

(k) Effect of variation of silver perchlorate concentration.

Temp. 85.0°C; $H_2$ pressure 4.0 atm.; 0.031 M. $HClO_4$

$0.83 \times 10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $AgClO_4 \times 10^2$ M. | $-\frac{d[H_2]}{dt} \times 10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\left.\frac{d[H_2]}{dt}\right]_{II} \times 10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 1.01 | 1.20 | 0.99 |
| 1.26 | 1.65 | 1.33 |
| 1.51 | 2.10 | 1.64 |
| 2.00 | 3.11 | 2.30 |
| 2.50 | 4.07 | 2.79 |
| 2.50 | 4.16 | 2.88 |
| 2.79 | 4.68 | 3.09 |

(l) Effect of variation of silver perchlorate concentration.

Temp. 100.8°C; $H_2$ pressure 4.0 atm.; 0.031 M. $HClO_4$

2.5 X $10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $AgClO_4$ X $10^3$ M. | $-\frac{d[H_2]}{dt}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\frac{d[H_2]}{dt}\Big]_{II}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 5.02 | 1.32 | 1.19 |
| 7.51 | 2.57 | 2.28 |
| 10.0 | 3.99 | 3.47 |
| 12.5 | 5.4 | 4.6 |
| 13.5 | 6.0 | 5.1 |
| 14.7 | 6.9 | 5.8 |

(m) Effect of variation of silver perchlorate concentration.

Temp. 120.3°C; $H_2$ pressure 4.0 atm.; 0.031 M. $HClO_4$

2.5 X $10^{-3}$ M. $Cr_2O_7^{=}$ initially

| $AgClO_4$ X $10^3$ M. | $-\frac{d[H_2]}{dt}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ | $-\frac{d[H_2]}{dt}\Big]_{II}$ X $10^7$ m.l.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 7.62 | 7.5 | 6.6 |
| 10.1 | 12.2 | 10.6 |
| 12.6 | 17.9 | 15.5 |
| 15.0 | 23.5 | 20.0 |

(n) Effect of variation of silver perchlorate concentration.

Temp. 110.0°C; 0.10 M. $HClO_4$; $1.67 \times 10^{-4}$ $Cr_2O_7^=$ initially

| $AgClO_4 \times 10^2$ M. | $k_o \times 10^5$ $sec.^{-1}$ | $k_1 \times 10^4$ $l.m.^{-1}sec.^{-1}$ |
|---|---|---|
| 0.763 | 0.35 | 0.57 |
| 1.006 | 0.94 | 1.13 |
| 1.255 | 2.04 | 1.96 |
| 1.530 | 3.77 | 3.13 |
| 1.674 | 5.19 | 3.88 |

(o) Effect of variation of silver perchlorate concentration.

Temp. 110.0°C; 0.03 M. $HClO_4$; $1.67 \times 10^{-4}$ $Cr_2O_7^=$ initially

| $AgClO_4 \times 10^2$ M. | $k_o \times 10^5$ $sec.^{-1}$ | $k_1 \times 10^4$ $l.m.^{-1}sec.^{-1}$ |
|---|---|---|
| 0.506 | 0.21 | 0.64 |
| 0.754 | 0.97 | 1.66 |
| 0.954 | 2.27 | 2.71 |
| 1.247 | 6.04 | 3.94 |

(p) Effect of variation of $HClO_4$ concentration.

Temp. 110.0°C; $9.6 \times 10^{-3}$ M. $AgClO_4$; $1.67 \times 10^{-4}$ M. $Cr_2O_7^=$ initially

| $HClO_4$ M. | $NaClO_4$ M. | $k_o \times 10^5$ $sec.^{-1}$ | $k_1 \times 10^4$ $l.m.^{-1}sec.^{-1}$ |
|---|---|---|---|
| 0.203 | 0.10 | 0.52 | 0.45 |
| 0.153 | 0.15 | 0.65 | 0.57 |
| 0.100 | 0.20 | 0.95 | 0.76 |
| 0.050 | 0.25 | 1.80 | 1.45 |
| 0.030 | 0.27 | 3.19 | 2.00 |

## REDUCTION OF PERMANGANATE BY HYDROGEN

(q) Effect of hydrogen partial pressure on permanganate reduction

Temp. 50.0°C; 0.30 M. $HClO_4$

| $P_{H_2}$ atm. | $-\frac{d\ln[MnO_4^-]}{dt}$ X $10^4$ sec.$^{-1}$ | k l.m.$^{-1}$sec.$^{-1}$ |
|---|---|---|
| 0 | (0.01) | - |
| 0.23 | 0.95 | 0.83 |
| 0.40 | 1.67 | 0.87 |
| 0.59 | 2.27 | 0.80 |
| 0.74 | 2.85 | 0.79 |
| 0.88 | 3.42 | 0.80 |

(r) Effect of temperature on rate of permanganate reduction

0.30 M. $HClO_4$ .

| Temp. °C | k l.m.$^{-1}$sec.$^{-1}$ |
|---|---|
| 30.0 | 0.19 |
| 40.0 | 0.40 |
| 45.0 | 0.56 |
| 60.0 | 1.66 |
| 70.0 | 3.08 |

(s) Effect of hydrogen pressure on the silver ion catalysed reduction of permanganate.

Temp. 40.0°C; 0.0184 M. $AgClO_4$; 0.30 M. $HClO_4$

| $P_{H_2}$ atm. | $-\frac{d\ ln[MnO_4^-]}{dt} \times 10^4$ sec.$^{-1}$ | k' l.m.$^{-1}$sec.$^{-1}$ | k l.m.$^{-1}$sec.$^{-1}$ | $k_c$ l.$^2$m.$^{-2}$sec.$^{-1}$ |
|---|---|---|---|---|
| 0 | (0.01) | - | | |
| 0.21 | 0.86 | 0.82 | 0.40 | 23 |
| 0.27 | 1.03 | 0.78 | 0.40 | 21 |
| 0.38 | 1.59 | 0.85 | 0.40 | 24 |
| 0.58 | 2.29 | 0.80 | 0.40 | 22 |
| 0.75 | 3.00 | 0.81 | 0.40 | 22 |
| 0.92 | 3.84 | 0.84 | 0.40 | 24 |

(t) Effect of variation of silver perchlorate concentration on the rate of reduction of permanganate.

Temp. 40.0°C; 0.30 M. $HClO_4$

| $AgClO_4 \times 10^3$ M. | k' l.m.$^{-1}$sec.$^{-1}$ | k l.m.$^{-1}$sec.$^{-1}$ | $k_c$ l.$^2$m.$^{-2}$sec.$^{-1}$ |
|---|---|---|---|
| 4.5 | 0.49 | 0.40 | 20 |
| 9.3 | 0.59 | 0.40 | 21 |
| 37.0 | 1.34 | 0.40 | 25 |
| 44.3 | 1.54 | 0.40 | 26 |
| 55.7 | 1.66 | 0.40 | 23 |
| 55.9 | 1.76 | 0.40 | 24 |

(u) Effect of temperature on the silver ion catalysed reduction of permanganate

$0.0184$ M. $AgClO_4$; $0.30$ M. $HClO_4$

| Temp.<br>°C | k'<br>$l.m.^{-1}sec.^{-1}$ | k<br>$l.m.^{-1}sec.^{-1}$ | $k_c$<br>$l.^2m.^{-2}sec.^{-1}$ |
|---|---|---|---|
| 30.0 | 0.45 | 0.19 | 14 |
| 45.0 | 1.10 | 0.56 | 30 |
| 50.0 | 1.48 | 0.81 | 37 |
| 60.0 | 2.74 | 1.66 | 58 |

## APPENDIX B

Sample calculation of exchange rate, using as illustration experiment B.

(1) Deuterium content of solution.

density of sample at 20° = 1.0200

corrected for air buoyancy = 1.0210

$\Delta d = 0.0228$

where d = density of sample
" $d_1$ = " " $H_2O$
" $d_2$ = " " $D_2O$
$\Delta d = d - d_1$

$$\text{wt. \% } D_2O = \frac{\Delta d}{d_1 + \Delta d} \; \frac{d_2}{d_2 - d_1} \times 100 = 23.0\%$$

2804 ml. of this $H_2O - D_2O$ mixture were used.

$\therefore$ wt. of $H_2O$ = 0.770 X 1.0210 X 2804 = 2204.4 gm.

(1.246 X 20) - 6.219 = 18.7 gm. ($H_2O$ in $AgClO_4$ soln.)

(1.544 X 9.6) - 9.04 = 5.9 gm. ($H_2O$ in $HClO_4$ soln.)

166.4 X 0.9982 = 164.1 gm. ($H_2O$ used to make volume to 3 l.)

Total $H_2O$ = 2393.1 gm.

wt. of $D_2O$ = 0.230 X 1.0210 X 2804 = 658.4 gm.

$\therefore$ No. moles $H_2O$ = 132.8
" " $D_2O$ = 32.9

$$\text{mole \% D} = 19.8 = \frac{D}{H + D} \times 100$$

(2) Calculation of "n".

$D_2 \mid D^+$, E° = - 3.4 mv. at 21°C.

$$\text{hence, } \frac{2.3\,RT}{F} \log \frac{P_{H_2}^{\frac{1}{2}} \; a_{D^+}}{P_{D_2}^{\frac{1}{2}} \; a_{H^+}} = -0.0034$$

or $$\frac{P_{D_2}\,[H^+]^2}{P_{H_2}\,[D^+]^2} = 1.31 = K_1 \qquad \text{assuming } f_{H^+} = f_{D^+}$$

$$K_2 = \frac{P_{H_2}\,[D_2O]}{P_{D_2}\,[H_2O]} = 13.5$$

$$\therefore \frac{[H^+]^2}{[D^+]^2} = 13.5 \times 1.31 \; \frac{[H_2O]}{[D_2O]}$$

$$K_3 = \frac{[HDO]^2}{[H_2O][D_2O]} = 3.78$$

Now $$H_2O \;+\; D_2O \;=\; 2\ HDO$$

$$(0.802 - \alpha) \quad (0.198 - \alpha) \qquad 2\alpha$$

$$\therefore \frac{4\alpha^2}{(0.198 - \alpha)(0.802 - \alpha)} = 3.78$$

$$\alpha = 0.157$$

$$\therefore \frac{[H^+]}{[D^+]} = 16.7$$

and $$n = \frac{[D^+]}{[D^+] + [H^+]} = 0.0564 \text{ at } 20°C.$$

(3) Calculation of x using equation $\Delta x = (r_o - r)\,\frac{v\ n\ RT}{V}\,\Delta t$

| Time Period<br>min. | $r_o - r$<br>m.l.$^{-1}$sec.$^{-1}$atm.$^{-1}$ | v<br>mean<br>l. | n | V<br>mean<br>l. | $\Delta t$<br>sec. | $\Delta x$ | x |
|---|---|---|---|---|---|---|---|
| 0-35 | $1.71 \times 10^{-7}$ | 2.97 | 0.0564 | 1.77 | $2.10 \times 10^{3}$ | 0.10 | 0.10 |
| 35-85 | $1.71 \times 10^{-7}$ | 2.95 | 0.0564 | 1.79 | $3.00 \times 10^{3}$ | 0.15 | 0.25 |
| 85-145 | $1.71 \times 10^{-7}$ | 2.93 | 0.0564 | 1.81 | $3.60 \times 10^{3}$ | 0.18 | 0.43 |

$$r_o = k_I\,[AgClO_4]^2[H_2] + k_{II}\,[AgClO_4][H_2]$$

$$r = k_I\,[AgClO_4]^2[H_2] + \frac{k_{II}\,[AgClO_4]^2[H_2]}{k'_{II}\,[HClO_4] + [AgClO_4]}$$

using $[AgClO_4] = 0.0100$ M.

$[HClO_4] = 0.0309$ M.

$T = 383.2°C$

$[H_2] = \frac{0.0188}{22.4}$ m.l.$^{-1}$

(4) Observed values of x

| Sample | mass 2 peak $(H_2^+)$ cm. | mass 3 peak X 30 $(H_3^+ + HD^+)$ cm. | Ratio X $10^2$ | correction * for $H_3^+$ | % HD x |
|---|---|---|---|---|---|
| B-1 | 13.8 | 0.80 | 0.193 | 0.144 | 0.05 |
| B-2 | 19.25 | 1.7 | 0.294 | 0.195 | 0.10 |
| B-3 | 13.55 | 1.4 | 0.344 | 0.142 | 0.20 |

---

* Determined from Fig. 48.

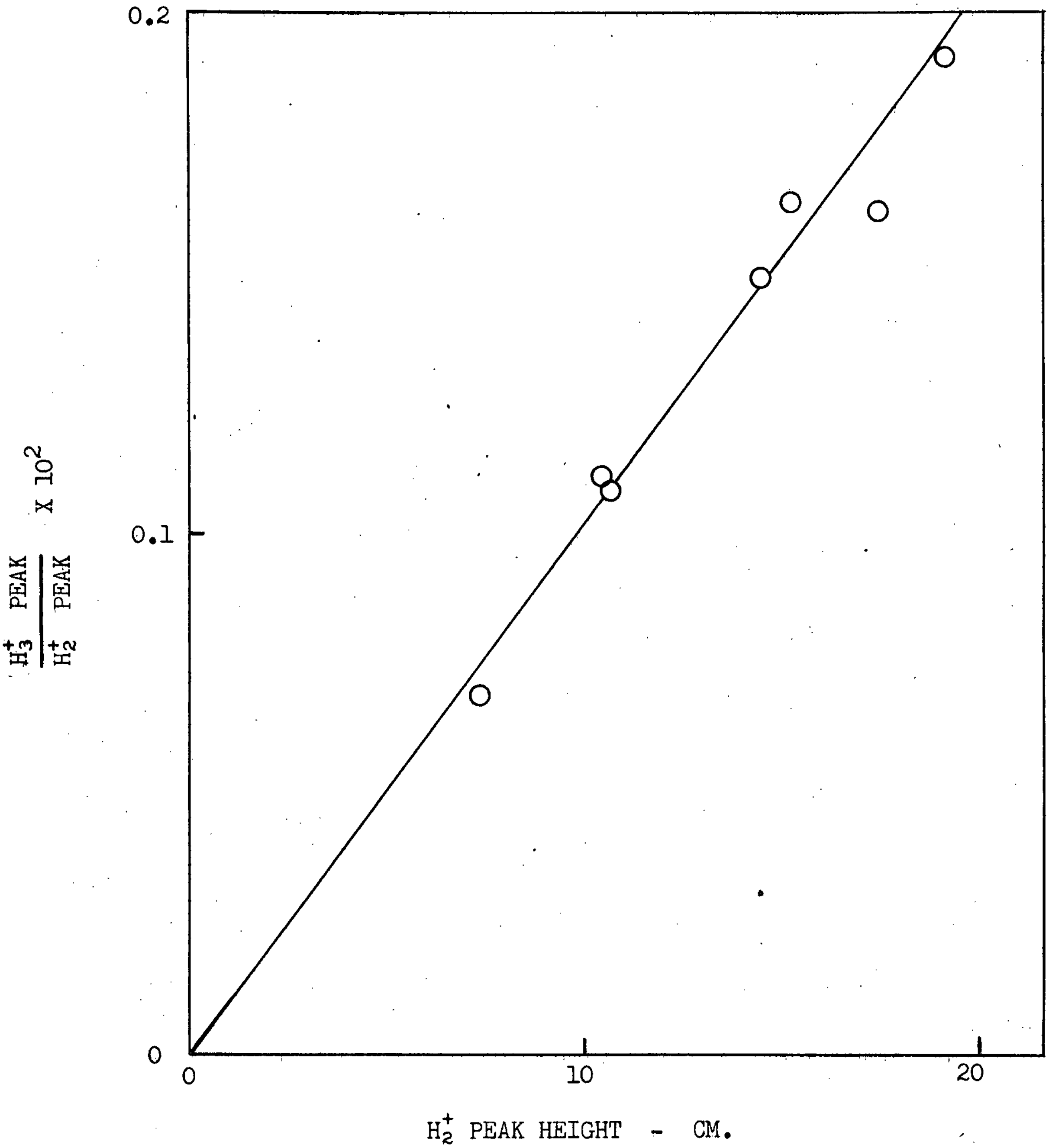


Fig. 48. Ratio of mass 3 peak / mass 2 peak plotted against mass 2 peak for ordinary hydrogen.

# APPENDIX C

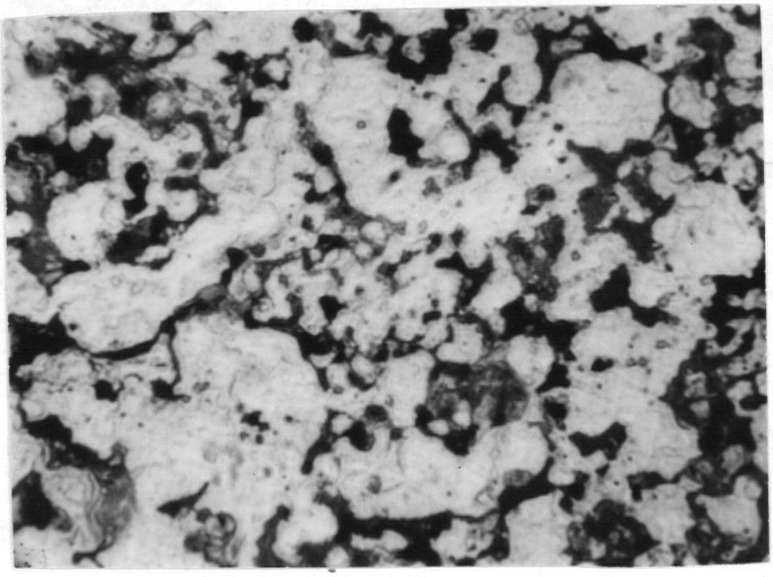
## X-ray crystallographic examination of the products precipitated from silver solutions by hydrogen.

X-ray diffraction patterns were determined by the Debye-Scherrer method using a copper target and nickel filter. The following results were obtained:

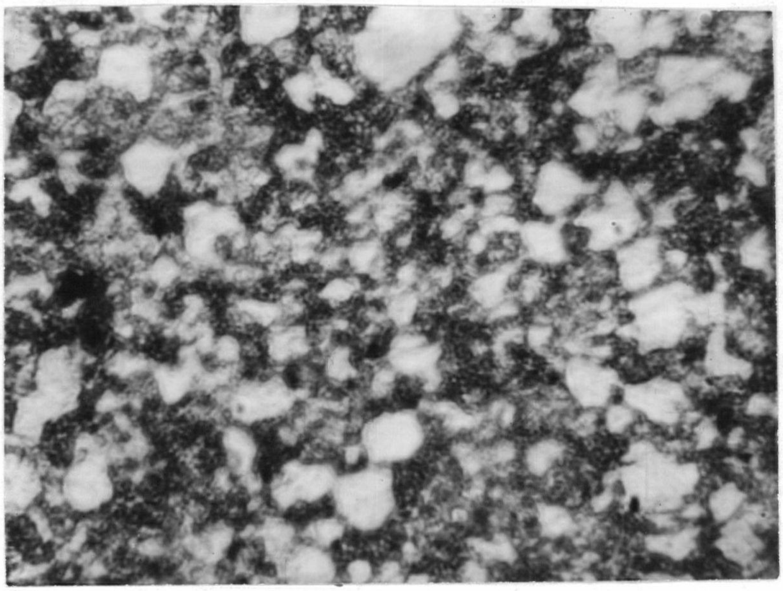
| Material | Structure | Lattice Parameter Å |
|---|---|---|
| Precipitate from perchlorate solution | FCC | 4.086 |
| Precipitate from acetate solution | FCC | 4.086 |
| Precipitate from EDA solution | FCC | 4.086 |
| Precipitate from EDA +NaOH solution | FCC | 4.086 |

The recorded lattice parameter for silver is 4.0856 Å (1). No lines other than those of the FCC pattern were observed.

(1) Barrett, C.S., "Structure of Metals", McGraw-Hill Publishing Co., New York, N.Y., 1952, p. 648.



(a) Silver precipitated from perchloric acid solution.
1560 X, KCN : $H_2O_2$ etch.



(b) Silver precipitated from ethylene diamine complex.
1560 X, KCN : $H_2O_2$ etch.

Fig. 49. Photomicrographs of precipitated silver.