

CARBON MONOXIDE REDUCTION

OF

AQUEOUS SILVER ACETATE

by

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B.Sc., Queen's University, 1957  
M.Sc., Queen's University, 1958

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF  
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The University of British Columbia,  
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PROGRAMME OF THE

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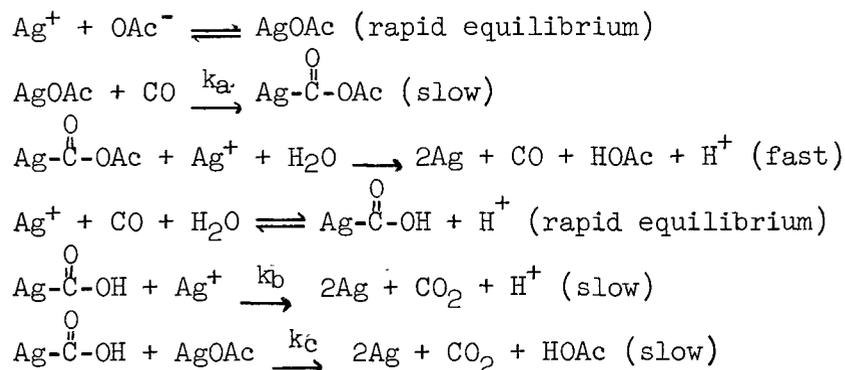
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GRADUATE STUDIES

ABSTRACT

The kinetics of the carbon monoxide reduction of silver perchlorate in sodium acetate - acetic acid buffered aqueous solution were studied between 60° and 110°C. by following the pressure decrease in a closed system. The reduction occurs homogeneously in the liquid phase by two parallel reaction paths, one of which is independent of pH. The second path is favoured by increased pH and has both an acetate-independent and an acetate-dependent component.

The observed kinetics are consistent with the formation of intermediate complexes by the insertion of a carbon monoxide molecule between a silver ion and a co-ordinated oxygen-donating base (e.g. OAc<sup>-</sup>, H<sub>2</sub>O) according to the following mechanism:



Silver-acetate complexes are about a factor of three more reactive than hydrated silver ions in the pH-dependent reaction. This enhanced reactivity is attributed to stabilization by the basic acetate anion of the proton released in the reduction process.

The effect of increasing pH on the reduction rate is much greater than the specific effects associated with silver-acetate complexing.

Field of Study: Metallurgy

Metallurgical Thermodynamics.....C.S. Samis  
Metallurgical Kinetics.....E. Peters  
Metallurgy of the Rarer Metals.....E. Peters  
Hydrometallurgy.....Staff  
Nuclear Metallurgy..... W.M. Armstrong

Other Studies:

Statistical Mechanics..... L.G. Harrison  
Surface Chemistry..... L.G. Harrison  
Chemical Kinetics..... J. Halpern and G.B. Porter  
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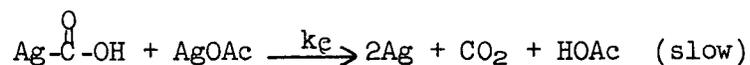
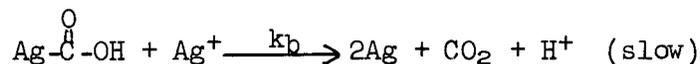
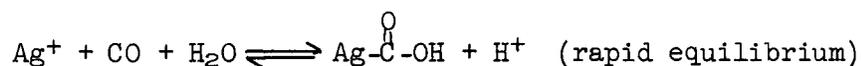
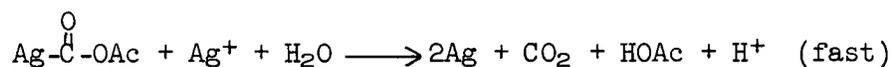
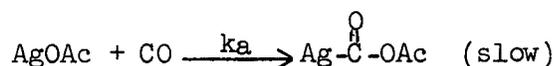
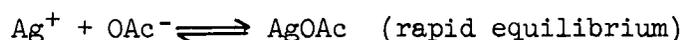
PUBLICATIONS

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I INTRODUCTIONI-1 General

Carbon monoxide, although it is a major by-product of many pyrometallurgical processes, finds little direct commercial use in current metallurgical operations. As a reducing agent carbon monoxide exerts a slightly greater potential than hydrogen, which is used commercially in the production of copper, nickel and cobalt powders from ammoniacal leach solutions (1,2), and therefore might be expected to find similar applications. The fact that carbon monoxide is not used in large-scale operations may be explained in part by a general aversion to this gas because of its toxicity and the perhaps mistaken concept that CO-reduction would lead to higher costs. This latter objection is not necessarily valid particularly in the vicinity of electric smelting plants where CO is produced in large volumes and available merely for the cost of collection. What is probably a more significant reason for its limited use is the general lack of detailed information regarding potentially useful CO-metal reactions.

The greatest use of CO in the metallurgical industry has been the production of elemental nickel by the Mond carbonyl process. The process consists essentially of reacting the gas with reduced nickel to form a nickel carbonyl which is then thermally decomposed to give a high purity nickel powder (3). A modification of the Mond process was used in Germany during World War II to produce nickel and iron for powder metallurgy applications (4). The carbonyl process has also been adapted to the recovery of iron and nickel from nickeliferous lateritic ores (5).

Perhaps the greatest potential use of CO in processes of metallurgical importance lies in the displacement of dissolved metals from hydrometallurgical

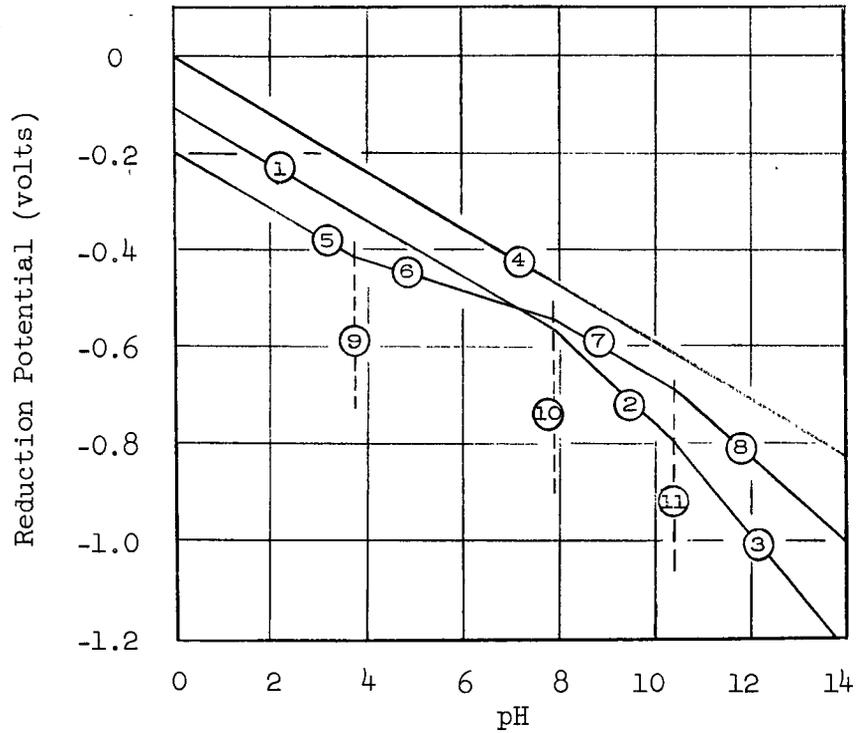
leach liquors. A process has been developed (6,7) for the production of elemental copper, nickel or cobalt powders from ammoniacal solutions under autoclave conditions, reduction being accomplished at somewhat lower temperatures than corresponding hydrogen reactions. In the production of nickel powder difficulties associated with carbonyl handling are a disadvantage. In the production of copper metal, however, CO is particularly useful because of its ability to stabilize the copper(I) species against hydrolysis thus preventing the precipitation of cuprous oxide and providing a purer product from a wider range of solution compositions.

A Russian process for the recovery of nickel has been described (8) in which nickel concentrates are leached in ammonia solution under oxygen pressure, and the resulting solution reduced with CO to form a carbonyl which is then decomposed to yield the nickel product.

## I-2 Thermodynamic Considerations of CO Reactions in Aqueous Solution

When CO acts as a reducing agent in aqueous solution it is oxidized to carbon dioxide, bicarbonate or carbonate, depending on the pH of the solution. The thermodynamic potentials of the corresponding couples at room temperature are depicted in Figure 1 in the form of a potential-pH diagram using the International or Stockholm Convention (9) for the sign of the electrode potentials. The associated potentials of formic acid and formate are also included together with that of the hydrogen electrode. In constructing the diagram, unit activity for all species except  $H^+$  has been assumed. The various reactions considered are listed in Figure 1 together with a summary of the thermodynamic expressions used. The details of the thermodynamic calculations are given in Appendix E.

It is apparent from the diagram that CO is a stronger reducing agent than  $H_2$  by at least 0.1 volts at all pH values. Thus CO might be expected to



- |   |                                 |
|---|---------------------------------|
| 1. $\text{CO}_2 + 2\text{H}^+ + 2\text{e} = \text{CO} + \text{H}_2\text{O}$         | $E = -0.103 - 0.059 \text{ pH}$ |
| 2. $\text{HCO}_3^- + 3\text{H}^+ + 2\text{e} = \text{CO} + 2\text{H}_2\text{O}$     | $E = 0.128 - 0.089 \text{ pH}$  |
| 3. $\text{CO}_3^{=} + 4\text{H}^+ + 2\text{e} = \text{CO} + 2\text{H}_2\text{O}$    | $E = 0.433 - 0.118 \text{ pH}$  |
| 4. $2\text{H}^+ + 2\text{e} = \text{H}_2$   | $E = -0.059 \text{ pH}$         |
| 5. $\text{CO}_2 + 2\text{H}^+ + 2\text{e} = \text{HCOOH}$                           | $E = -0.198 - 0.059 \text{ pH}$ |
| 6. $\text{CO}_2 + \text{H}^+ + 2\text{e} = \text{HCOO}^-$                           | $E = -0.309 - 0.030 \text{ pH}$ |
| 7. $\text{HCO}_3^- + 2\text{H}^+ + 2\text{e} = \text{HCOO}^- + \text{H}_2\text{O}$  | $E = -0.079 - 0.059 \text{ pH}$ |
| 8. $\text{CO}_3^{=} + 3\text{H}^+ + 2\text{e} = \text{HCOO}^- + \text{H}_2\text{O}$ | $E = 0.227 - 0.089 \text{ pH}$  |
| 9. $\text{HCOOH} = \text{H}^+ + \text{HCOO}^-$                                      | $\text{pH} = -\log K = 3.8$     |
| 10. $\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$                | $\text{pH} = -\log K = 7.8$     |
| 11. $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{=}$                                 | $\text{pH} = -\log K = 10.4$    |

Figure 1. Potential-pH Diagram for the Oxidation of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{HCOOH}$  and  $\text{HCOO}^-$  at  $25^\circ\text{C}$

reduce several metal ions which are not reducible by  $H_2$ . However, cobalt with a standard reduction potential of -0.277 volts (10) is the least noble metal reported to be reduced by CO (6) and it is also reduced by  $H_2$  (1,2,6). In both cases reduction of ammonia complexes can be accomplished in basic or slightly acidic solutions. Other metals which have been produced by CO-reduction include nickel (6,8,11,12), bismuth (12), copper (6,13), silver (13,14), mercury (15) and gold (16). Some metal species which are not reducible to metal by CO can be reduced to a lower oxidation state as in the reduction of permanganate to  $MnO_2$  in acid or neutral solutions and to  $MnO_4^-$ , which gives  $Mn^{++}$  by disproportionation, in basic solution (15,17). Chromate is reduced to  $Cr_2O_3$  in acid solutions (18). The reduction potential of CO can be increased by raising the CO partial pressure, a hundred-fold increase being equivalent to 2 pH units or about 0.1 volts at room temperature. Higher temperatures increase the pressure dependence of the CO potential as well as increasing the reaction rates.

Figure 1 indicates that formic acid or the formate ion is a stronger reducing agent than CO in acid solution while the reverse is true at higher pH values, the equipotential point occurring at about pH 7 at room temperature. Thus it is possible for CO to react with certain basic salt solutions to form metal formates. Thermodynamically, the most favourable cases include the hydroxides of the alkali metals and the alkali earths except beryllium (19). The reaction has been known since the original synthesis of sodium formate from sodium hydroxide in the mid-nineteenth century (20).

The standard reduction potential of the oxygen electrode in acid solution is 1.229 volts (10) and thus the CO-reduction of  $H_2O$  to form  $CO_2$  and  $H_2$  is thermodynamically favourable. This is the water-gas shift reaction familiar in the gas phase at elevated temperatures. It has also been observed in basic aqueous solutions at temperatures greater than  $150^\circ C$  (21).

### I-3 Structure of Carbon Monoxide and its Compounds

The CO molecule contains a total of 14 electrons, 6 from the carbon atom (i.e.  $1s^2 2s^2 2p^2$  in the ground state) and 8 from the oxygen atom (i.e.  $1s^2 2s^2 2p^4$  in the ground state) and is best described as a triply-bonded structure as is  $N_2$ , which is isoelectronic with CO. In terms of the molecular orbital (MO) treatment the CO structure is described (22) by



The  $z\sigma$  orbital is a non-bonding MO represented largely by the O(2s) atomic orbital (AO);  $y\sigma$  represents a sigma-antibonding MO of C(2s) and O(2p<sub>x</sub>);  $x\sigma$  is a non-bonding MO represented largely by the C(2p<sub>x</sub>) AO;  $w\pi$  represents two degenerate pi-bonding MO's of C(2p<sub>y</sub>) and O(2p<sub>y</sub>). The bonds formed by the  $y\sigma$  and  $w\pi$  MOs give CO its triple-bond structure. Two degenerate pi-antibonding MO's ( $v\pi$ ) are associated with  $w\pi$  and it is these orbitals which are largely responsible for the stability of metal carbonyl complexes.

The lone pair of electrons in the CO( $x\sigma$ ) orbital (which corresponds to the C(2p<sub>x</sub>) AO) are donated to a metal atom and form a sigma-bond when a carbonyl complex is formed\*. Stabilization of the complex occurs through pi-bonding between occupied metal d-orbitals and the empty  $v\pi$  pi-antibonding orbitals of CO thus providing a mechanism for the removal of the excess charge which would otherwise be present on the metal atom. The pi-acceptor and sigma-donor characteristic of CO complement each other and permit the formation of stable complexes even though CO itself is a poor donor as shown by its inability to form strong complexes with empty orbital acceptors (24).

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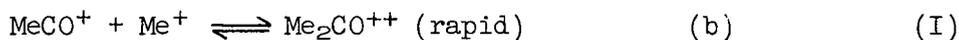
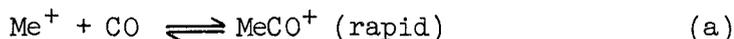
\* The lone pair of electrons in the CO( $z\sigma$ ) MO, which corresponds to the O(2s) AO, apparently is not donated (23) because O is much more electronegative than C. Donation of electrons in the CO( $w\pi$ ) MO's is not observed experimentally although this type of donation is observed with certain other ligands which are isoelectronic with CO (e.g. acetylene)(23).

Carbonyl compounds are formed with transition metals in groups VI, VII and VIII of the periodic table (25,26). Carbon monoxide is also absorbed by cuprous chloride in ammoniacal solution, by silver sulphate in concentrated sulphuric acid, by mercuric acetate in methyl alcohol, and by dry auric chloride (25).

In the Fischer-Tropsch synthesis CO and H<sub>2</sub> react in the presence of a suitable metal catalyst to yield primary alcohols, olefins and saturated hydrocarbons, the relative yields depending on the operating conditions (27). When olefins are added to the CO-H<sub>2</sub> gas mixtures, alcohols, aldehydes and ketones are produced and the process is known as the OXO or hydroformylation synthesis (28). The OXO synthesis requires a cobalt catalyst (in the metallic, salt or carbonyl form) while catalysts for the Fischer-Tropsch synthesis include cobalt, nickel, iron and other metals capable of forming metal carbonyls. The role of these catalysts is associated with their ability to form metal carbonyls and related complexes which act as intermediates in the organic reactions (29). The mechanisms for these and other syntheses involve the insertion of CO into metal-carbon and metal-oxygen bonds (29).

#### I-4 Kinetics of Metal Ion Reduction by Carbon Monoxide in Aqueous Solution

The rate of CO-reduction of both Ag<sub>2</sub>SO<sub>4</sub> and CuSO<sub>4</sub> has been reported (13) to be first-order in CO partial pressure up to at least 60 atm and second-order in dissolved metal. The following mechanism was proposed to account for the observed kinetics:



In the silver studies two series of measurements were made with initial Ag<sub>2</sub>SO<sub>4</sub>

concentrations between about 0.007 and 0.03 M, one series being buffered with 0.65 M  $\text{NH}_4\text{OAc}^*$  and the other unbuffered. The rate law for the buffered series between 70 and 110°C is given as:

$$-d[\text{Ag(I)}]/dt = 6.02 \times 10^4 [\text{Ag(I)}]^2 P_{\text{CO}} \exp(-9300/RT) \quad (\text{M min}^{-1})$$

and for the unbuffered series between 70 and 150°C as:

$$-d[\text{Ag(I)}]/dt = 12.8 \times 10^5 [\text{Ag(I)}]^2 P_{\text{CO}} \exp(-14,100/RT) \quad (\text{M min}^{-1})$$

Thus at 90°C the reaction rate in the buffered system is about 36 times faster than in the unbuffered system.

The reduction rate of  $\text{CuSO}_4$  was measured in dilute unbuffered solutions, apparently to minimize corrosion and hydrolysis problems. Also a sheet of copper metal, etched to give a high surface area, was required to obtain reproducible results. The reported rate law as measured between 160 and 190°C has the form:

$$-d[\text{Cu(total)}]/dt = 2.56 \times 10^{13} [\text{Cu(total)}]^2 P_{\text{CO}} \exp(-33,500/RT) \quad (\text{M min}^{-1})$$

Another kinetic study involving the CO-reduction of aqueous silver amines in basic solution has recently been reported (14). Measurable rates were readily obtained at atmospheric pressure and room temperature and were shown to be consistent with the rate law:

$$-d[\text{CO}]/dt = k_{\text{exp}}[\text{CO}][\text{AgL}_2^+]/[\text{HL}^+]$$

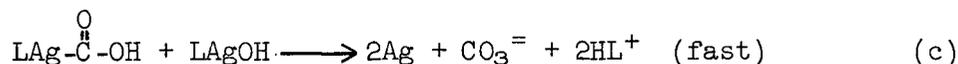
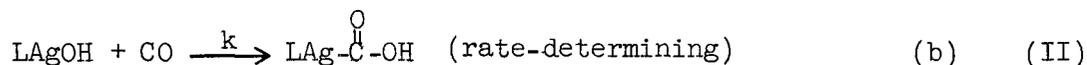
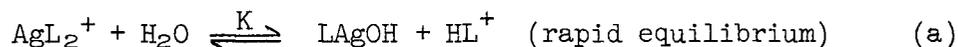
where L denotes an amine ligand. This rate law is equivalent to:

$$-d[\text{CO}]/dt = k[\text{CO}][\text{LAgOH}]$$

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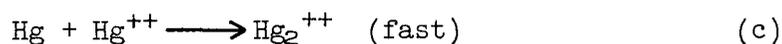
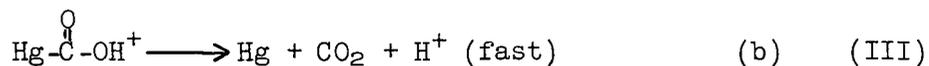
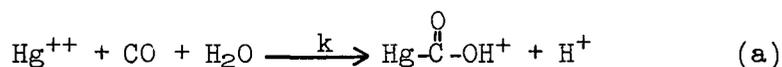
\*  $\text{OAc}^-$  is used throughout the text to denote the acetate radical  $\text{CH}_3\text{COO}^-$ .

The experimental rate constant  $k_{\text{exp}}$  is thus equivalent to  $kK_dK_bK_h$ , where  $K_d$  is the first instability constant of  $\text{AgL}_2^+$ ,  $K_b$  is the basicity constant of the amine and  $K_h$  is the association constant of  $\text{AgL}^+$  with  $\text{OH}^-$ . The following mechanism was proposed to account for the observed kinetics:



For the ligands  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{NH}_2$  and  $(\text{C}_2\text{H}_5)_2\text{NH}$  variations in  $k_{\text{exp}}$  were almost wholly accounted for by variations in  $K_dK_b$  while  $kK_h$  remained essentially independent of the nature of the amine and had a value of about  $10^5 \text{ M}^{-2} \text{ sec}^{-1}$  at  $25^\circ\text{C}$ . At  $[\text{NH}_4^+]$  greater than about 0.02 M with  $\text{NH}_3$  as the ligand (14a) departures from the above rate law were observed which were explained by the slowing down of reaction II(c), due to lower  $[\text{LAgOH}]$ , until competition between II(c) and the reverse of II(b) controlled the rate. On the basis of these findings it was concluded (14) that high pH rather than specific complexing effects is responsible for the high reactivity of Ag(I) toward CO in amine-buffered aqueous solutions.

Additional support for the nature of the proposed intermediate in the rate-determining step II(c) was drawn (14) by analogy from the mechanism developed from a parallel study (15) to describe the CO-reduction of  $\text{Hg}^{++}$  in dilute perchloric acid, viz:



The observed kinetics at atmospheric pressure over the temperature range 26 to 54°C were found to be consistent with the rate law:

$$-d[\text{CO}]/dt = k[\text{CO}][\text{Hg}^{++}]$$

with a  $\Delta H^\ddagger$  of 14.6 kcal/mole and a  $\Delta S^\ddagger$  of -13 e.u. The structure of the proposed intermediate in the rate-determining step III(a) is analogous to the stable methyl formate derivative  $\text{AcO}-\text{Hg}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$  which is formed when CO reacts with methanolic solutions of mercuric acetate under similar conditions (30). It was suggested (15) that the rate-determining step involves the insertion of CO between  $\text{Hg}^{++}$  and a co-ordinated water molecule. Similar reactions involving the insertion of CO into metal-oxygen bonds are important in a number of metal carbonyl catalytic reactions (29).

The kinetics of the CO-reduction of  $\text{MnO}_4^-$  (15), as measured in aqueous solution at atmospheric pressure over the temperature range 28 to 50°C and the pH-range 1 to 13, are consistent with the rate law:

$$-d[\text{CO}]/dt = k[\text{CO}][\text{MnO}_4^-]$$

with a  $\Delta H^\ddagger$  of 13 kcal/mole and a  $\Delta S^\ddagger$  of -17 e.u. The reduction is strongly catalyzed by  $\text{Ag}^+$  or  $\text{Hg}^{++}$  (15) and in dilute perchloric acid solutions the rate law is:

$$-d[\text{CO}]/dt = k[\text{CO}][\text{MnO}_4^-][\text{X}]$$

where X represents  $\text{Ag}^+$  or  $\text{Hg}^{++}$ . For  $\text{Ag}^+$ ,  $\Delta H^\ddagger = 1.2$  kcal/mole and  $\Delta S^\ddagger = -31$  e.u.; for  $\text{Hg}^{++}$ ,  $\Delta H^\ddagger = 6.4$  kcal/mole and  $\Delta S^\ddagger = -21$  e.u. It is suggested (15) that the high catalytic activity in these reactions may be due to intermediates of the type  $\text{Ag}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OMnO}_3$  and  $\text{Hg}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OMnO}_3^+$ .

The kinetics of the CO-reduction of  $\text{Bi}_2(\text{SO}_4)_3$  at pH's between 0.4 and -0.7 are described by the rate law (12):

$$-d[\text{Bi(III)}]/dt = 8.2 \times 10^6 [\text{Bi(III)}] P_{\text{CO}} ([\text{H}^+]^{-1} - 0.24) \exp(-23,000/RT) \text{ (M min}^{-1}\text{)}$$

The high acid concentrations are required to prevent hydrolysis. It was suggested (12) that the active species is  $\text{BiOH}^{++}$ . An induction period which decreases with increasing initial  $[\text{Bi(III)}]$  indicates that the reaction is heterogeneous.

The rate law for the CO-reduction of  $\text{Ni(OAc)}_2$  in  $\text{HOAc} - \text{NH}_4\text{OAc}$  (0.5 M) buffered solution at constant pH of 5.3 is given (12) as:

$$-d[\text{Ni(II)}]/dt = 80.6 [\text{Ni(II)}] (P_{\text{CO}} - 5.2) \exp(-12,000/RT) \text{ (M min}^{-1}\text{)}$$

Other studies on the reduction of nickel(II) amine sulphate complexes (11,21) indicate that the rate increases with increasing pH. The CO dependence may reflect a thermodynamic influence on the rate.

### I-5 Object and Scope of the Present Investigation

This thesis embodies the results of a kinetic study of the CO-reduction of aqueous  $\text{AgOAc}$  and  $\text{AgClO}_4$  in acid solution. The work forms part of a general investigation of the mechanisms by which CO displaces metals from aqueous salt solutions.

At the time the study was undertaken the only published information on the kinetics of the reaction was that of the CO-reduction of  $\text{Ag}_2\text{SO}_4$  solutions (13). At  $90^\circ\text{C}$  the rates measured in  $\text{NH}_4\text{OAc}$  buffered solution were some 36 times greater than the corresponding rates in unbuffered sulphate solution. Initial experiments in the present study revealed large pH effects on the reduction rate of  $\text{AgClO}_4$  and  $\text{AgOAc}$  in acid solution. The previously proposed mechanism (see mechanism I, Section I-4), however, takes no account of pH effects. Also the possible variation in reactivity of different  $\text{Ag(I)}$  complexes (e.g.  $\text{Ag}^+$ ,  $\text{AgSO}_4^-$ ,  $\text{AgOAc}$ ,  $\text{AgNH}_3$ ,  $\text{Ag(NH}_3)_2$ ,  $\text{Ag(NH}_3)_2\text{OH}$ , etc.) was not

considered. At the concentrations used in the  $\text{Ag}_2\text{SO}_4\text{-NH}_4\text{OAc}$  studies (13) it is estimated, from reported room temperature complexity constants (31) that more than 60% of the silver was complexed with ammonia. The simpler system of  $\text{AgClO}_4$ , generally buffered with  $\text{NaOAc}$  and  $\text{HOAc}$ , was chosen to further elucidate the mechanism by which CO displaces silver from aqueous solution.

A preliminary study of the CO-reduction of  $\text{Cu(OAc)}_2$  and  $\text{Cu(ClO}_4)_2$  was also made. The first step in the reaction apparently is the reduction of Cu(II) to Cu(I) which forms a stable complex with CO and then hydrolyzes to precipitate a  $\text{Cu}_2\text{O}$  product. It was demonstrated that both aqueous  $\text{Cu(OAc)}_2$  and  $\text{Cu(ClO}_4)_2$  catalyze the oxidation of CO by  $\text{O}_2$ , measurable rates being obtained above  $125^\circ\text{C}$ . The catalyzed reaction is first-order in CO and zero-order in  $\text{O}_2$ , and occurs homogeneously in the liquid phase in a similar manner to the  $\text{CuSO}_4$ - and  $\text{Cu(ClO}_4)_2$ -catalyzed oxidation of  $\text{H}_2$  by  $\text{O}_2$  (32). The rate increases with increasing  $[\text{Cu(II)}]$  and pH but the exact dependence was not determined. The CO-Cu(II) reaction is currently the subject of another study in these laboratories.

No catalytic activity of aqueous  $\text{AgClO}_4$  or  $\text{AgOAc}$  in the CO- $\text{O}_2$  reaction was detected at temperatures to  $150^\circ\text{C}$ , although at  $250^\circ\text{C}$   $\text{Ag}_2\text{SO}_4$  is reported (32) to catalyze the  $\text{H}_2\text{-O}_2$  reaction, possibly by a heterogeneous process.

## II EXPERIMENTAL

### II-1 Reactor System

Reduction experiments were conducted for the most part in a small (approximately 120 ml) pressure vessel, the rate of reaction generally being followed by the decrease of pressure in a closed system. In some cases, however, rates were determined by analyzing periodic liquid samples. The pressure vessel and associated fittings were manufactured from stainless steel (type 316) by Pressure Products Industries Inc., Hatboro, Pennsylvania and designed for working pressures up to 7200 psi. A schematic diagram of the reactor system is given in Figure 2 and a section drawing of the reactor is shown in Figure 3. Pressure-tight closure of the vessel was achieved by using a totally enclosed stainless steel Flexitellic gasket having a Teflon and asbestos filler. Agitation was provided by mounting the reactor in a vertical position on a shaker mechanism which when activated reciprocated horizontally at 275 oscillations per minute with a 1-1/2-in stroke.

Gas inlet and outlet lines of flexible 1/16-in o.d. stainless steel (type 347) capillary tubing, and a stainless steel clad 1/16-in o.d. iron-constantan thermocouple were connected through the bottom of the reactor by means of Ermeto stainless steel (type 17-4 PH) sleeve fittings. Also a short 1/8-in o.d. liquid sampling line was connected through the bottom of the vessel.

### II-2 Pressure Measurement

The pressure of the system was measured with a Consolidated Electroynamics Corp. pressure transducer pick-up (type 4-311) mounted in the gas inlet line. The transducer consisted essentially of strain-gauge windings

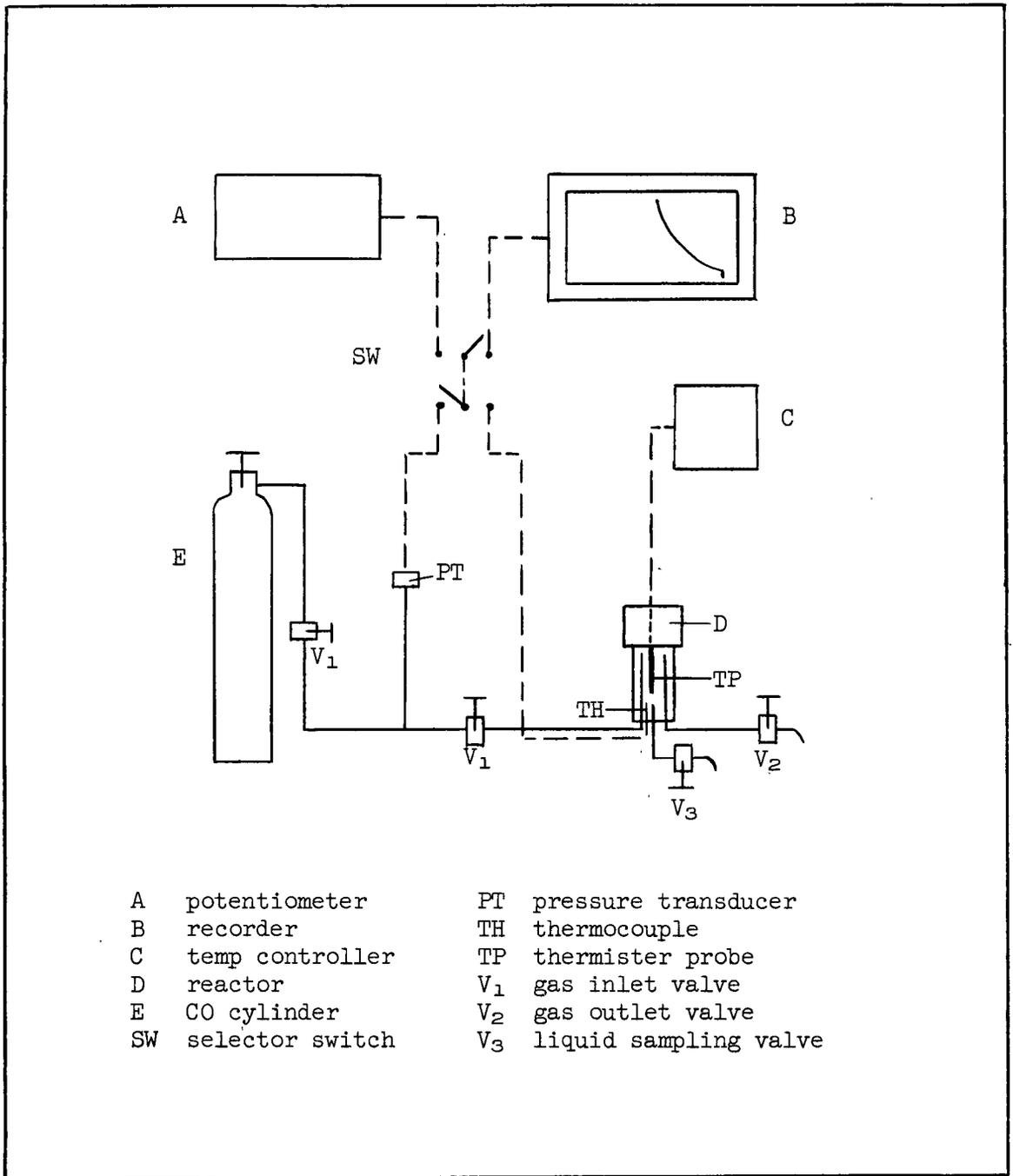


Figure 2. Schematic Diagram of Reactor System

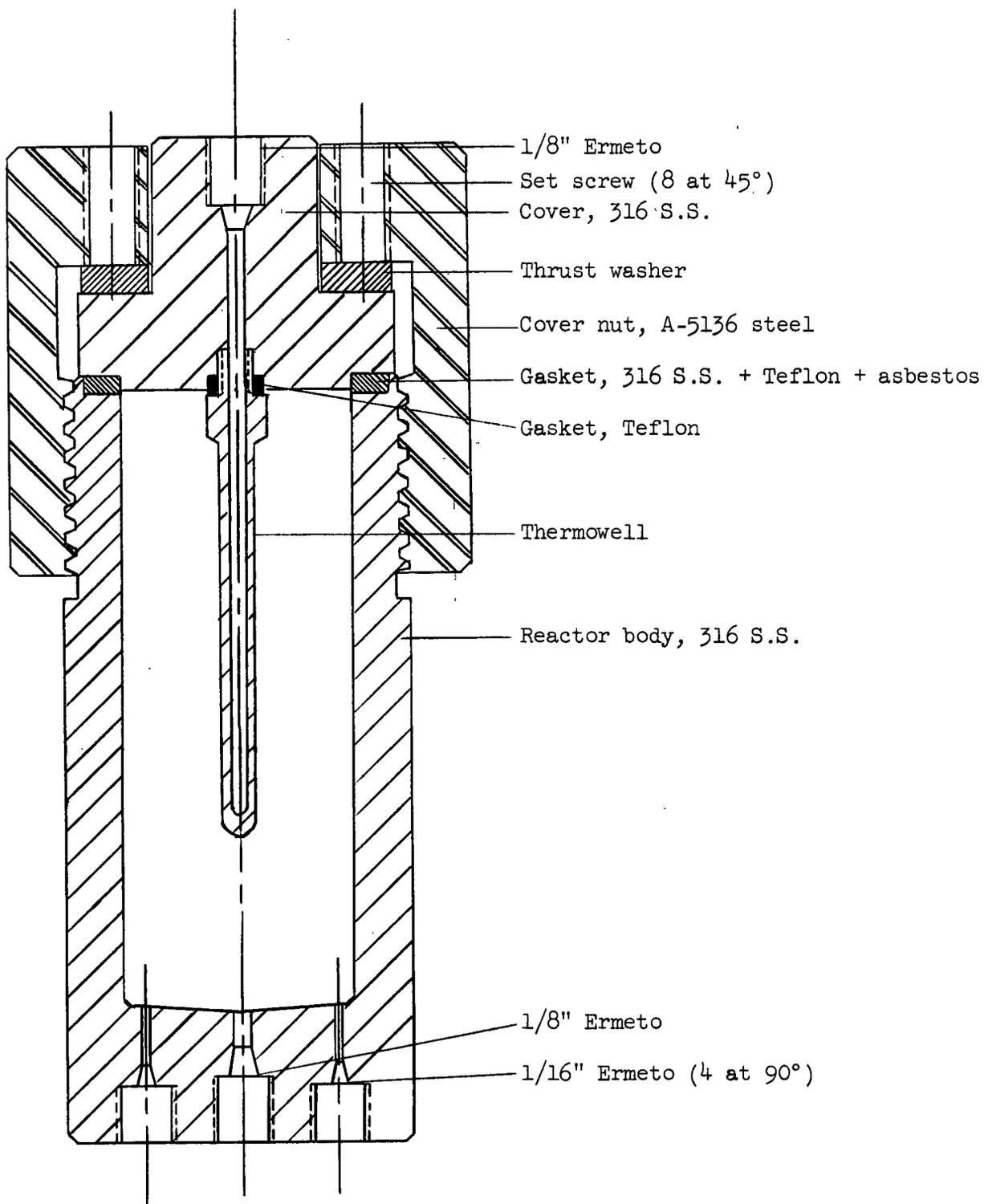


Figure 3. Stainless Steel Reactor (full-scale)

connected in a four-arm bridge circuit. Pressure against a diaphragm displaced the sensing element which changed the resistance of the two active arms and produced an electrical output proportional to the applied pressure. The bridge circuit was excited by a battery of dry cells supplying up to five volts at 10 ma, and the output was measured with a high precision Leeds and Northrup potentiometer (No. 7552) or recorded on a 10 mv Brown Electronik strip-chart recorder. Three transducers were available covering the ranges 0-150, 0-500 and 0-1000 psig, each of which had been calibrated at an excitation voltage of 5.0 volts dc by the manufacturer and had a nominal 20 mv full-scale output. From the manufacturer's specifications it is estimated that the pressure measurements had an accuracy of better than 2%.

### II-3 Temperature Control and Measurement

The temperature of the experimental solution was regulated to  $\pm 0.3^{\circ}\text{C}$  using a Yellow Springs Instrument Co. Thermistemp Temperature Controller (Model 71) with a stainless steel clad thermister probe (No. 406) mounted in a thermo-well in the reactor lid. The heating unit was a 600-watt external band heater connected to a variable transformer through the controller which was shunted by a four-ohm nichrome resistor when in the "off" position. Regulation was made by adjustment of the transformer to give a heat input sufficient to maintain the temperature at a value slightly below the operating point when the regulator was in the "off" position, and slightly above the operating point when the regulator was in the "on" position. The top of the reactor was wrapped with removable asbestos lagging to reduce heat losses.

Independent temperature measurements were made with an iron-constantan thermocouple sheathed in stainless steel inserted through the bottom of the reactor. The thermocouple was calibrated at the melting point of indium ( $156.4^{\circ}\text{C}$ ), the steam point and at room temperature by comparison with a

precision mercury-in-glass thermometer graduated in tenths of a degree.

#### II-4 Materials

All chemicals were of reagent grade and used without further purification. Carbon monoxide (99.5% min) was obtained from the Matheson Co. Analysis of several gas samples indicated that  $N_2$ ,  $O_2$  and  $H_2$  impurities were less than 0.2%, 0.1% and 0.002% respectively.

Experimental solutions were prepared by mixing and diluting aliquots of standard stock solutions.  $AgClO_4$  solutions were filtered after preparation and thus any trace amounts of  $Cl^-$  or  $ClO_3^-$  impurity were removed as insoluble  $AgCl$ .  $NaOAc$  and  $HOAc$  solutions were prepared with known weights of reagent and were not standardized further.

#### II-5 Chemical Analysis

Silver solutions were analyzed by titration in dilute nitric acid with standard ammonium thiocyanate using ferric nitrate as an indicator (33). Samples drawn during an experiment were filtered before analysis.

All pH measurements were made at room temperature with a Beckman pH-meter (Model G).

Gas samples were generally analyzed in a Beckman GC-1 chromatograph using molecular sieve and silica gel columns.

#### II-6 General Experimental Procedure

In general, the experimental procedure was to pipette a known volume (90-100 mls) of solution into the reactor, seal and heat to the desired temperature with the shaking mechanism operating. When temperature control had been achieved the shaking mechanism was stopped briefly while  $CO$  was added

to the desired pressure which usually required between 30 and 60 seconds. The pressure record indicated that CO equilibrium between the liquid and gaseous phase was attained within two to four minutes after agitation had been resumed.

Rates for reactions involving the reduction of  $\text{AgClO}_4$  in HOAc-NaOAc buffered solutions were generally measured by a pressure-drop method in which the decrease in pressure of the closed reactor system was recorded. The majority of the rate data was obtained by measuring the slope of each pressure-time record after CO saturation was complete (two to four minutes). These slope measurements were converted to rates expressed as  $\text{M sec}^{-1}$ \* using CO and  $\text{CO}_2$  solubility data and the estimated volumes of gas and liquid in the reactor. Corrections were made to the concentrations of  $\text{AgClO}_4$ , HOAc, NaOAc and CO to take account of the small amount of reaction which occurred during the initial CO saturation. The derivation of the mathematical expression used to convert the slope measurements to fundamental rate units is given in Appendix A.

To augment meager published data (34) the solubility of CO in water was measured from room temperature to  $220^\circ\text{C}$  at pressures to 63 atm. The technique and results of these measurements are given in Appendix B together with some data on the solubility of  $\text{H}_2$  in water measured under similar conditions. Also included are a few measurements on the solubility of  $\text{CO}_2$  in water and HOAc-NaOAc solutions at  $90^\circ\text{C}$  and 2.6 atm.

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\* All concentrations are expressed in terms of litres measured at room temperature ( $20\text{-}25^\circ\text{C}$ )

### III RESULTS AND DISCUSSION

#### III-1 Rate of Carbon Monoxide Reduction of Silver(I)

Early experiments demonstrated that at low pH the reduction of  $\text{AgClO}_4$  solutions was very slow even at temperatures of  $175^\circ\text{C}$  and CO pressures of 20 atm. When the solutions were buffered with NaOAc and HOAc, however, the rates were readily measured under much milder conditions (e.g.  $60^\circ\text{C}$  and 5 atm CO) by the pressure-drop method. Table I summarizes the rate of reaction between CO and Ag(I) as measured over a wide range of experimental conditions.

A set of typical pressure-time records is shown in Figure 4. The fast initial decrease in pressure corresponds to saturating the solution in CO and the slower pressure decrease thereafter corresponds to chemical reaction exclusively. The marked difference in the rate of pressure drop in the two regions of the curve is clear evidence that after initial CO saturation the measured rate of CO consumption is effectively independent of mass transfer of CO between the gas and liquid phases.

The rates measured from the initial slopes of pressure-time records were estimated to have possible errors of at least  $\pm 10\%$  in favourable cases and these errors may have risen to  $\pm 20\%$  or higher for faster or slower rates. The reproducibility of the rates, however, was generally better than  $\pm 5\%$  as shown in Table II. Results included in the table also indicate that the rate is independent of the surface area of stainless steel and precipitated silver in contact with the solution. The reaction therefore is not heterogeneous in nature but must occur homogeneously in the liquid phase. No effect on the rate was detected when the  $\text{CO}_2$  concentration present at the time the initial slopes were measured was increased a factor of five. The presence of small amounts of air (equivalent to about one atmosphere) was also without

TABLE I

Reduction Rate of Silver(I) by CO Under Various  
Experimental Conditions

Temp °C	[Ag(I)] M	[NaOAc] M	[Acid] M	P <sub>CO</sub> atm	R x 10 <sup>6</sup> <sup>a</sup> M s <sup>-1</sup>	Method <sup>b</sup>
175	.03	--	.05 <sup>c</sup>	20	0.36 <sup>e</sup>	[Ag(I)]
90	.05	--	.002 <sup>c</sup>	53	0.58 <sup>f</sup>	pH
90	1.0	--	.05 <sup>c</sup>	53	12.0 <sup>f</sup>	pH
60	.10	.13	.77 <sup>d</sup>	5.4	0.95 <sup>g</sup>	Pressure
60	.10	.13	.05 <sup>d</sup>	5.3	3.81 <sup>g</sup>	Pressure
80	.11	.19	.06 <sup>d</sup>	5.4	18.5 <sup>g</sup>	Pressure
90	.04	.66	.10 <sup>d</sup>	12.4	41.4 <sup>g</sup>	Pressure
90	.24	.04	.77 <sup>d</sup>	27.1	83.0 <sup>g</sup>	Pressure
110	.11	.27	.28 <sup>d</sup>	4.6	40.8 <sup>g</sup>	Pressure
110	.10	.18	.05 <sup>d</sup>	4.5	93.7 <sup>g</sup>	Pressure

a -  $R = -d[CO]/dt = -0.5d[Ag(I)]/dt = -0.5d[H^+]/dt$

b - [Ag(I)] = silver analysis of periodic liquid samples

pH = pH determination of periodic liquid samples

Pressure = pressure-drop method

c - Present as HClO<sub>4</sub>

d - Present as HOAc

e - Average rate between 2 and 15 hours

f - Average rate after 15 minutes

g - Initial rate after CO saturation complete (2-4 minutes)

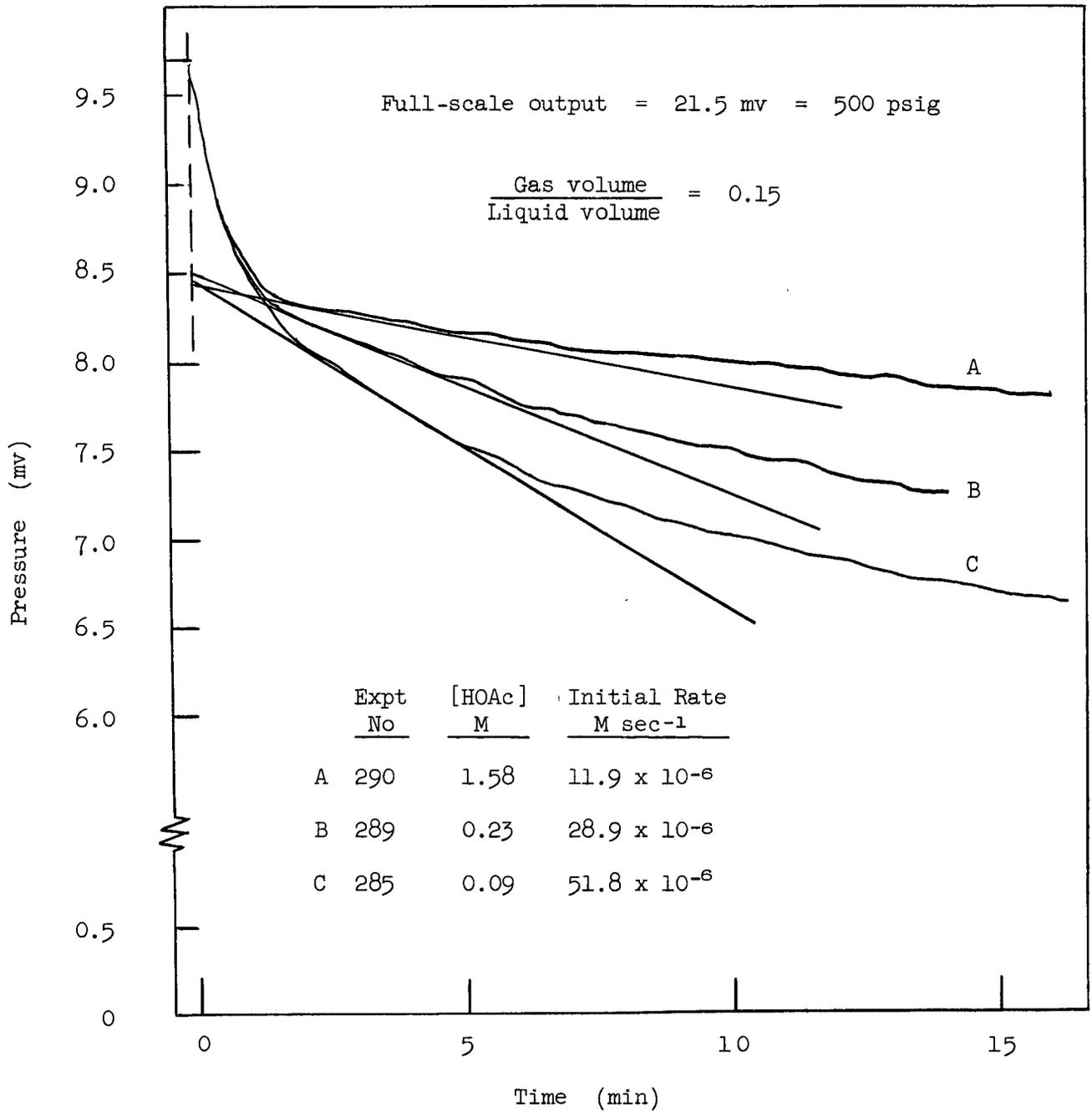


Figure 4. Typical Pressure-Time Records (0.235 M AgClO<sub>4</sub>; 0.090 M NaOAc; 11.7 atm CO; 90°C)

TABLE II

Reproducibility of Rate Measurements

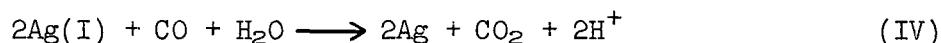
Expt No	Temp °C	Initial Concentrations				R x 10 <sup>6</sup> M s <sup>-1</sup>	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	Average Deviation %
		[AgClO <sub>4</sub> ] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm			
139	90	.100	.090	.180	26.6	21.4	.804	6.2
140	90	.100	.090	.180	26.7	20.2	.755	-0.3
141	90	.100	.090	.180	26.3	18.7	.711	-6.1
161	90	.115	.045	.766	27.7	14.4	.520	1.8
164 <sup>a</sup>	90	.115	.045	.766	27.5	14.2	.516	1.0
165 <sup>b</sup>	90	.115	.045	.766	25.6	12.7	.496	-2.9
265	90	.144	.195	.195	5.16	19.4	3.75	-3.9
264 <sup>c</sup>	90	.144	.195	.195	5.10	20.9	4.09	4.9
266 <sup>d</sup>	90	.144	.195	.195	5.04	20.3	4.02	3.1
267 <sup>e</sup>	90	.144	.195	.195	4.78	18.5	3.87	-0.8
268 <sup>f</sup>	90	.144	.195	.195	5.04	18.9	3.75	-3.9
198	110	.115	.195	.023	4.49	124.	27.6	9.1
200	110	.115	.195	.023	4.53	111.	24.6	-2.8
201	110	.115	.195	.023	4.49	106.	23.7	-6.3

- a - Contained 0.1 g Ag precipitated during previous experiment plus 2.0 g silver sponge obtained from the Consolidated Mining and Smelting Co. Ltd.
- b - Reactor thoroughly leached with HNO<sub>3</sub> prior to charging to remove all traces of previously precipitated Ag.
- c - Air evacuated from solution in reactor prior to heat-up.
- d - Added CO<sub>2</sub> to 5.7 psi prior to CO addition.
- e - Contained 3.3 g fine 316 S.S. filings.
- f - Contained 1.0 g Ag precipitated during previous experiments plus 3.0 g silver sponge obtained from the Consolidated Mining and Smelting Co. Ltd.

effect on the rate.

### III-2 Chemistry and Stoichiometry of the Reaction

When dissolved silver undergoes reduction by carbon monoxide in acid solution the reaction products are silver metal and carbon dioxide according to the reaction:



The Ag(I)-CO-CO<sub>2</sub> stoichiometry of reaction IV was examined at several temperatures by analyzing liquid and gas samples taken after about 50-60% reaction had occurred. Solution composition and experimental conditions that gave relatively fast reduction rates were selected. The concentrations of CO and CO<sub>2</sub> were estimated from their partial pressures using solubility coefficients given in Appendix B, and assuming ideal gas laws. The results of these measurements, as summarized in Table III, agree within 10% with the stoichiometry represented by reaction IV\*. No H<sub>2</sub> was detected in any gas sample.

Several filtered liquid samples of reaction products were tested for the presence of aldehydes and ketones using 2,4-dinitrophenylhydrazine (35), and for compounds containing a CH<sub>3</sub>CO group using the Iodoform test (36,37). Liquid samples were analyzed qualitatively in a Beckman GC-2 chromatograph containing a Carbowax 1000 column using a thermal conductivity bridge detector, and also in a Perkin-Elmer Vapor Fractometer (Model 154C) containing a dinonyl phthalate column using a flame ionization detector\*\*. No organic compounds

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\* The metallic silver precipitate from a typical experiment was confirmed by X-ray diffraction. Mr. D.J. Rose performed the analysis and his assistance is gratefully acknowledged.

\*\* Thanks are extended to Professors C.A. McDowell and J. Halpern of the U.B.C. Chemistry Department for allowing these analyses to be performed in their laboratories.

TABLE III

Stoichiometry of Acetate-Buffered CO - Silver Perchlorate Reaction

Expt No	Temp °C	Initial Concentrations				[Ag(I)] Consumed M	[CO] Consumed M	[CO <sub>2</sub> ] Produced M	$\frac{\Delta[\text{Ag(I)}]}{\Delta[\text{CO}]}$	$\frac{\Delta[\text{CO}_2]}{\Delta[\text{CO}]}$
		[HOAc] M	[NaOAc] M	[Ag(I)] M	P <sub>CO</sub> atm					
228	90	--	0.222	0.115	5.44	0.069	0.037	0.038	1.9	1.0
229	110	0.039	0.195	0.115	4.42	0.073	0.038	0.041	1.9	1.1
224	120	0.023	0.195	0.115	4.08	0.064	0.035	0.036	1.8	1.0
225	120	0.023	0.195	0.115	4.08	0.063	0.035	0.039	1.8	1.1
226	120	--	0.222	0.115	4.08	0.061	0.031	0.035	2.0	1.1

except HOAc and NaOAc were detected.

In the absence of Ag(I) no CO absorption was observed beyond the amount initially required for saturation of the aqueous solutions. The presence of previously precipitated silver metal had no effect on the CO absorption in Ag(I)-free solutions. In the absence of CO no reduction of Ag(I) was detected in HOAc-NaOAc solutions over a period of several hours at 90°C.

These observations are consistent with the absence of side reactions affecting the CO-reduction of  $\text{AgClO}_4$  in NaOAc-HOAc buffered solutions and also with the stoichiometry represented in reaction IV.

### III-3 Effect of Carbon Monoxide Pressure

Figure 5\* shows that the reduction rate is directly proportional to CO partial pressure up to at least 30 atm. The CO partial pressures were estimated by subtracting the vapour pressure of  $\text{H}_2\text{O}$  and the partial pressure of air from the initial saturation pressure. Small corrections were also made to take account of the reaction which occurred during CO saturation. The deviations from Henry's law for the solubility of CO in  $\text{H}_2\text{O}$  at 30 atm have been estimated to be only a few per cent (see Appendix B) and since the possible errors in the initial rate measurements were between  $\pm 10$  and 20%, the reduction rate is proportional to the concentration of CO in solution, within experimental error. Figure 5 also indicates that the rate is favoured by a low HOAc/NaOAc ratio or by a high NaOAc concentration, or both.

### III-4 Effect of Acetic Acid

In view of the large variation in rate with pH (Table I) and HOAc/NaOAc ratio (Figure 5) a series of experiments was conducted over a wide

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\* Data for rates shown in Figures and Tables throughout the text are tabulated in Appendix D.

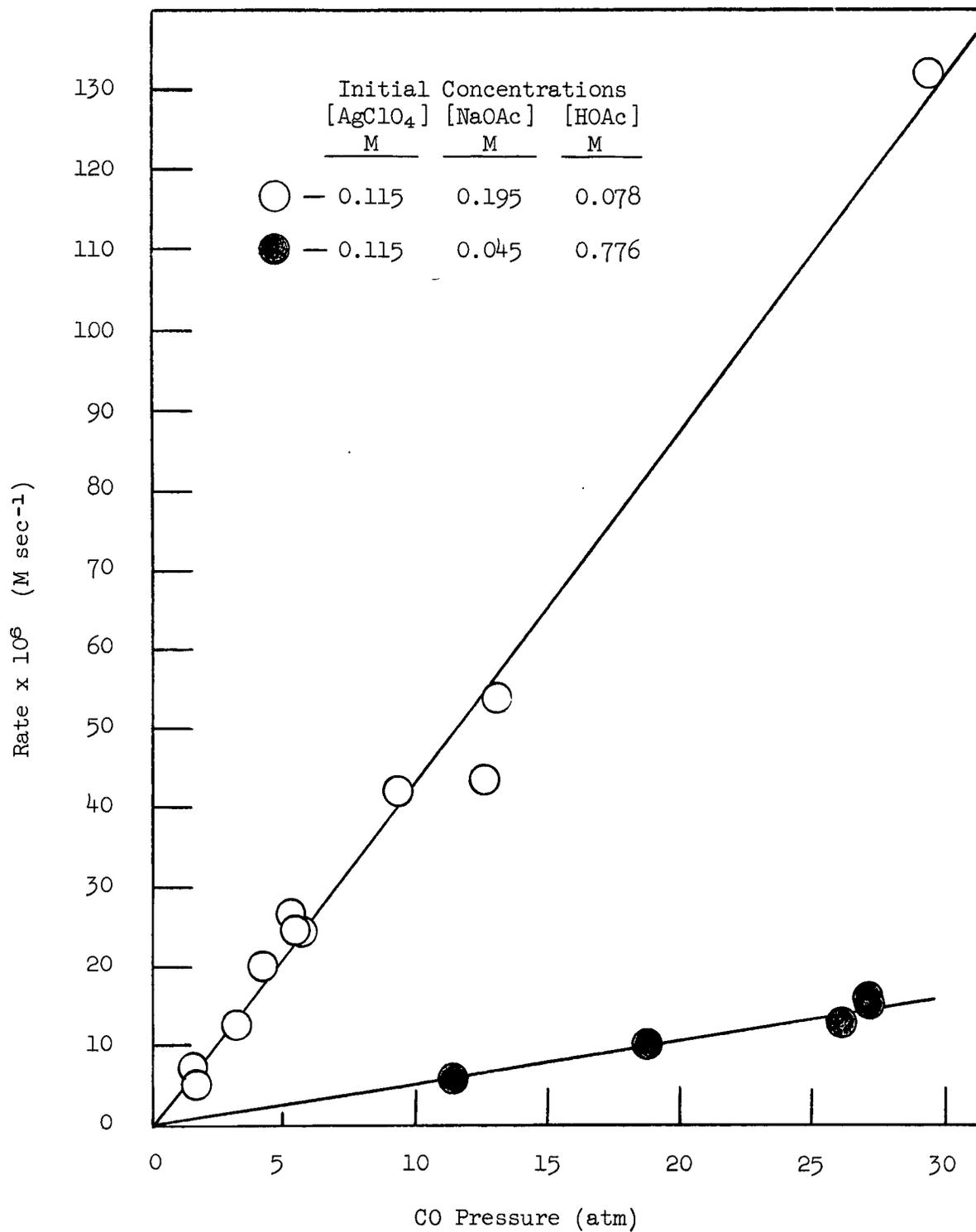


Figure 5. Dependence of Rate on CO Pressure (90°C)

range of HOAc concentrations at constant amounts of added NaOAc and AgClO<sub>4</sub>. The amount of free acetate initially present was therefore identical in each experiment and [H<sup>+</sup>] was directly proportional to [HOAc] through the relation:

$$[H^+] = K_i \frac{[HOAc]}{[OAc^-]} \quad (1)$$

where K<sub>i</sub> is the ionization constant of HOAc. The results of this series of experiments, as depicted in Figure 6, indicate that the rate (reduced to unit pressure\*) is inversely proportional to [HOAc]. The non-zero intercept of R' vs [HOAc]<sup>-1</sup> on the R'-axis indicates that there is also an acid-independent contribution to the overall rate. Therefore at a constant degree of silver-acetate complexing (i.e. constant amounts of added AgClO<sub>4</sub> and NaOAc) the apparent rate law is:

$$R = -d[CO]/dt \quad (2)$$

$$= I' P_{CO} + S' P_{CO}/[HOAc] \quad (3)$$

$$R' = R/P_{CO} \quad (4)$$

$$= I' + S'/[HOAc] \quad (5)$$

$$= I' + D' \quad (6)$$

where R' = total rate of CO consumption at unit pressure (M atm<sup>-1</sup> sec<sup>-1</sup>)

I' = acid-independent contribution to the total rate at unit pressure  
and constant complexing (M atm<sup>-1</sup> sec<sup>-1</sup>)

\* Since it has been demonstrated in Section III-3 that the rate is directly proportional to the partial pressure of CO, rates referred to in the remainder of the text have generally been reduced to unit pressure and represented as R' (i.e. R' =  $\frac{-d[CO]}{dt} / P_{CO} = R/P_{CO}$  M atm<sup>-1</sup> sec<sup>-1</sup>).

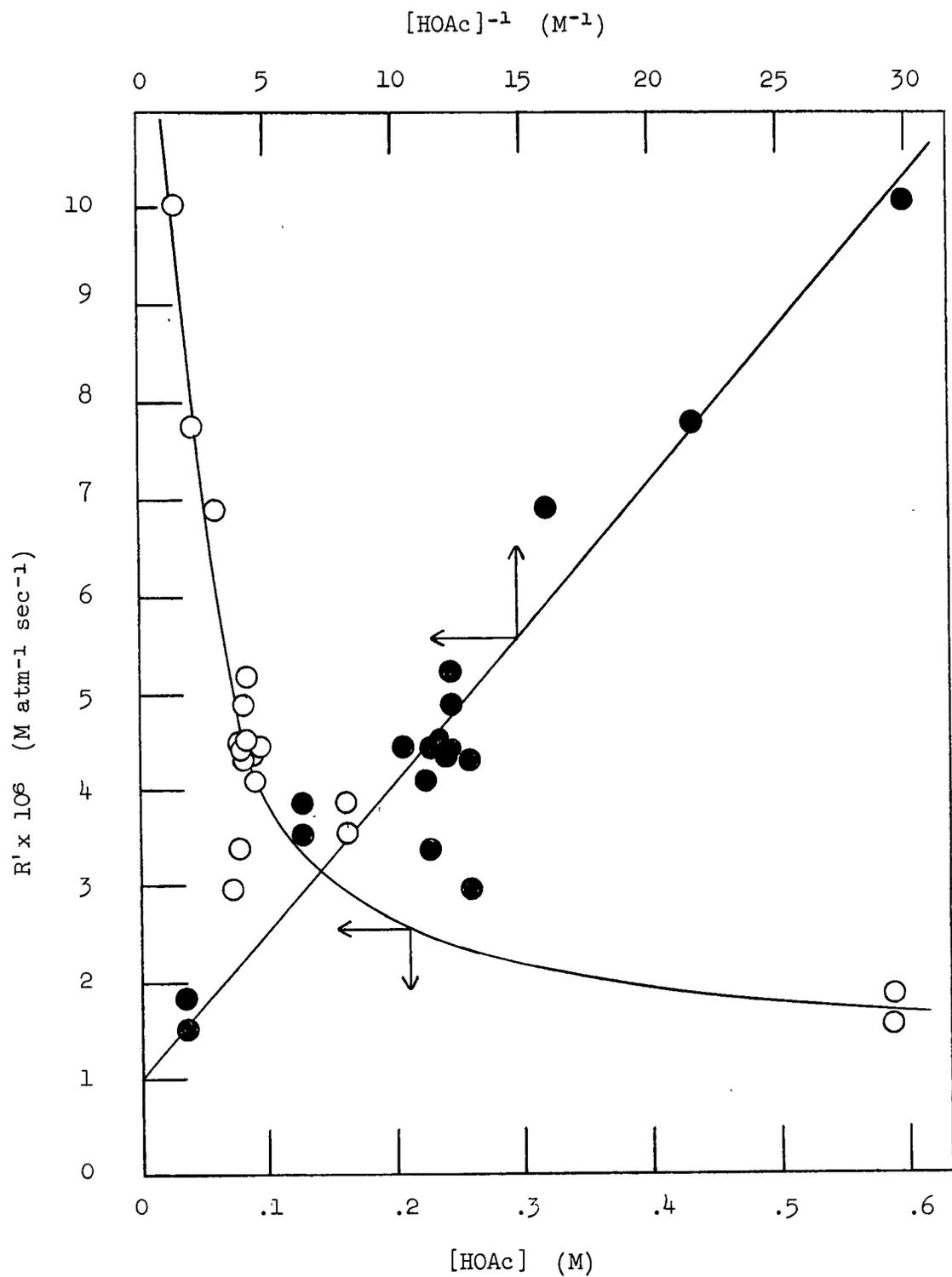


Figure 6. Dependence of Rate on  $[\text{HOAc}]$  and  $[\text{HOAc}]^{-1}$   
(0.115 M  $\text{AgClO}_4$ ; 0.195 M  $\text{NaOAc}$ ;  $90^\circ\text{C}$ )

$D'$  = acid-dependent contribution to the total rate at unit pressure and constant complexing ( $M \text{ atm}^{-1} \text{ sec}^{-1}$ )

$S'$  = acid-proportionality constant for the acid-dependent contribution to the total rate at unit pressure and constant complexing ( $M^2 \text{ atm}^{-1} \text{ sec}^{-1}$ ).

In terms of this nomenclature  $I'$  and  $S'$  are respectively the intercept and slope of  $R'$  vs  $[\text{HOAc}]^{-1}$  plots at constant complexing (e.g. Figures 6, 7 and 8).

Since the experimental solutions were buffered, an inverse dependence of  $R'$  on  $[\text{HOAc}]$  at constant degree of complexing corresponds to an inverse dependence on  $[\text{H}^+]$  or a direct dependence on  $[\text{OH}^-]$  for the acid-dependent contribution to the rate. This effect is similar to that reported for the CO-reduction of aqueous basic silver amine solutions at room temperature and atmospheric pressure (14). In these amine solutions no pH-independent contribution to the reduction rate was observed.

### III-5 Effect of Acetate Complexing

The effect on the rate of varying the amount of NaOAc added at constant  $\text{AgClO}_4$  addition is shown in Figure 7 while the effect of varying the amount of  $\text{AgClO}_4$  added at constant NaOAc is shown in Figure 8. The intercepts ( $I'$ ) and slopes ( $S'$ ) increase with increasing amounts of NaOAc and  $\text{AgClO}_4$  indicating that the overall rate is favoured by complexing between silver and acetate. Data of  $R'$  vs  $[\text{HOAc}]^{-1}$  at  $90^\circ\text{C}$  were obtained for fifteen different degrees of silver-acetate complexing as summarized in Table IV.

### III-6 Acid-Independent Reaction

A plot of the intercept ( $I'$ ) from  $R'$  vs  $[\text{HOAc}]^{-1}$  plots against the

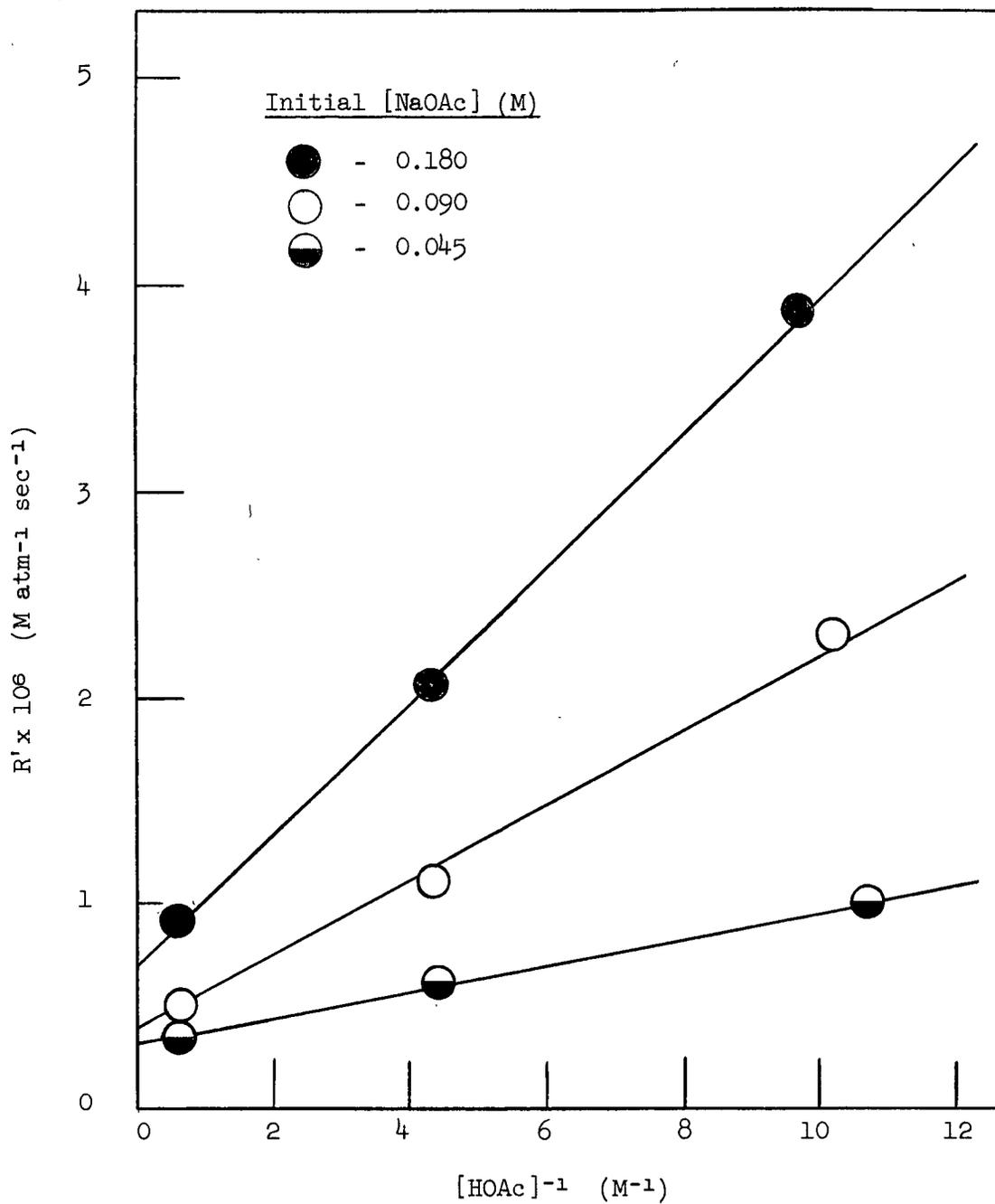


Figure 7. Dependence of Rate on  $[\text{HOAc}]^{-1}$  at Various NaOAc Levels (0.117 M  $\text{AgClO}_4$  initially; 12 atm CO; 90°C)

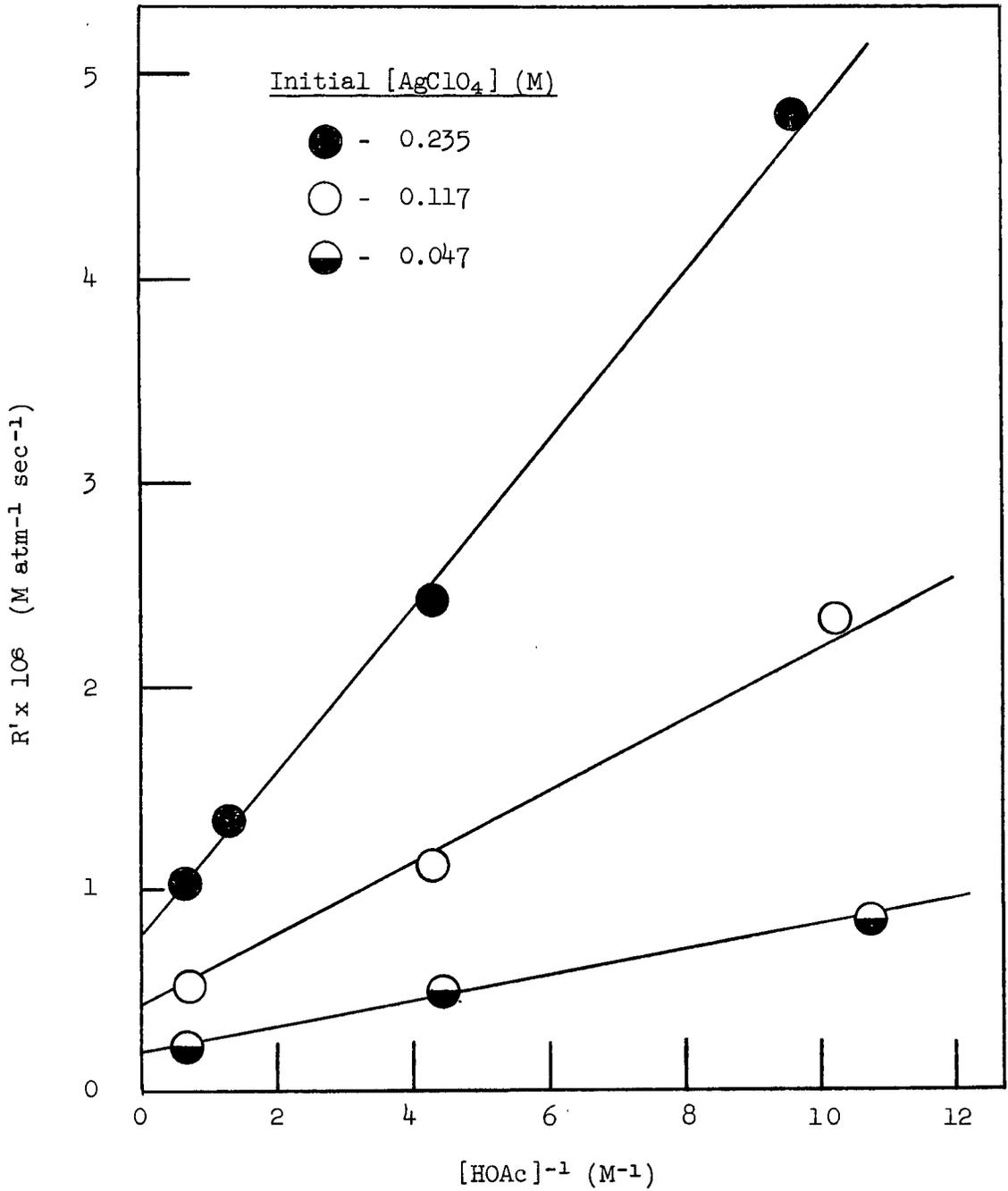


Figure 8. Dependence of Rate on  $[\text{HOAc}]^{-1}$  at Various  $\text{AgClO}_4$  Levels (0.090 M NaOAc; 12 atm  $\text{CO}$ ;  $90^\circ\text{C}$ )

TABLE IV

Summary of Intercepts and Slopes from  $R'$  vs  $[HOAc]^{-1}$  Plots  
at Various Degrees of Acetate Complexing \*

Series Code	No of Expts	[Ag(I)] M	[NaOAc] M	[Ag(I)][NaOAc] M <sup>2</sup>	$I' \times 10^6$ M a <sup>-1</sup> s <sup>-1</sup>	$S' \times 10^6$ M <sup>2</sup> a <sup>-1</sup> s <sup>-1</sup>
A	5	.048	.041	.0020	.15	.017
B	4	.096	.041	.0039	.31	.026
C	3	.045	.089	.0040	.22	.058
D	3	.115	.043	.0050	.32	.066
E	4	.090	.080	.0072	.40	.074
F	3	.044	.178	.0078	.43	.081
G	4	.042	.215	.0090	.43	.077
H	3	.230	.041	.0094	.50	.133
I	3	.114	.087	.0099	.44	.178
J	4	.225	.082	.0185	.78	.384
K	3	.110	.173	.0190	.70	.322
L	18	.110	.190	.0209	.90	.320
M	3	.040	.670	.0268	.87	.249
N	3	.056	.554	.0310	.85	.275
O	5	.056	.776	.0435	1.10	.340

\* Concentrations of Ag(I) and NaOAc are the averages of the corrected values of all experiments in a particular  $R'$  vs  $[HOAc]^{-1}$  series as tabulated in Appendix D.

total [Ag(I)] at various NaOAc levels produces a group of non-linear curves passing through the origin, as shown in Figure 9. When I' is plotted against [NaOAc] at various Ag(I) levels a similar set of curves is obtained, as shown in Figure 10. Combining the two sets of curves by plotting I' vs [Ag(I)][NaOAc], as in Figure 11, produces a single curve which passes through the origin and approaches an asymptote with increasing [Ag(I)][NaOAc]. This evidence suggests that the rate-determining step in the acid-independent reaction involves a CO molecule and a complex between Ag<sup>+</sup> and OAc<sup>-</sup>.

The total concentration of silver complexed with acetate can be approximated by an average value for the concentration of undissociated AgOAc molecules (i.e.  $\overline{[AgOAc]}$ ), which are the most abundant silver-acetate complexes present in the solutions studied\*. The acid-independent contribution to the rate law at unit pressure might then be expressed as:

$$I' = k_1' \overline{[AgOAc]} \quad (7)$$

$$= k_1' K_a [Ag^+] [OAc^-] \quad (8)$$

where  $K_a$  is the average stability constant of  $\overline{AgOAc}$ . Substituting for  $[Ag^+]$  in terms of total [Ag(I)],  $K_a$  and free  $[OAc^-]$  gives\*\*:

$$I' = k_1' K_a \frac{[Ag(I)][OAc^-]}{1 + K_a [OAc^-]} \quad (9)$$

or upon rearrangement:

$$\frac{[Ag(I)]}{I'} = \frac{1}{k_1' K_a [OAc^-]} + \frac{1}{k_1'} \quad (10)$$

\* Based on available stability constant data at room temperature (38) the ratio of AgOAc to  $Ag(OAc)_2^-$  is about 5:1 at 0.2 M NaOAc.

\*\*  $\overline{[AgOAc]} = K_a [Ag^+] [OAc^-] = [Ag(I)] - [Ag^+]$   
 $\therefore [Ag^+] = [Ag(I)] / (1 + K_a [OAc^-])$

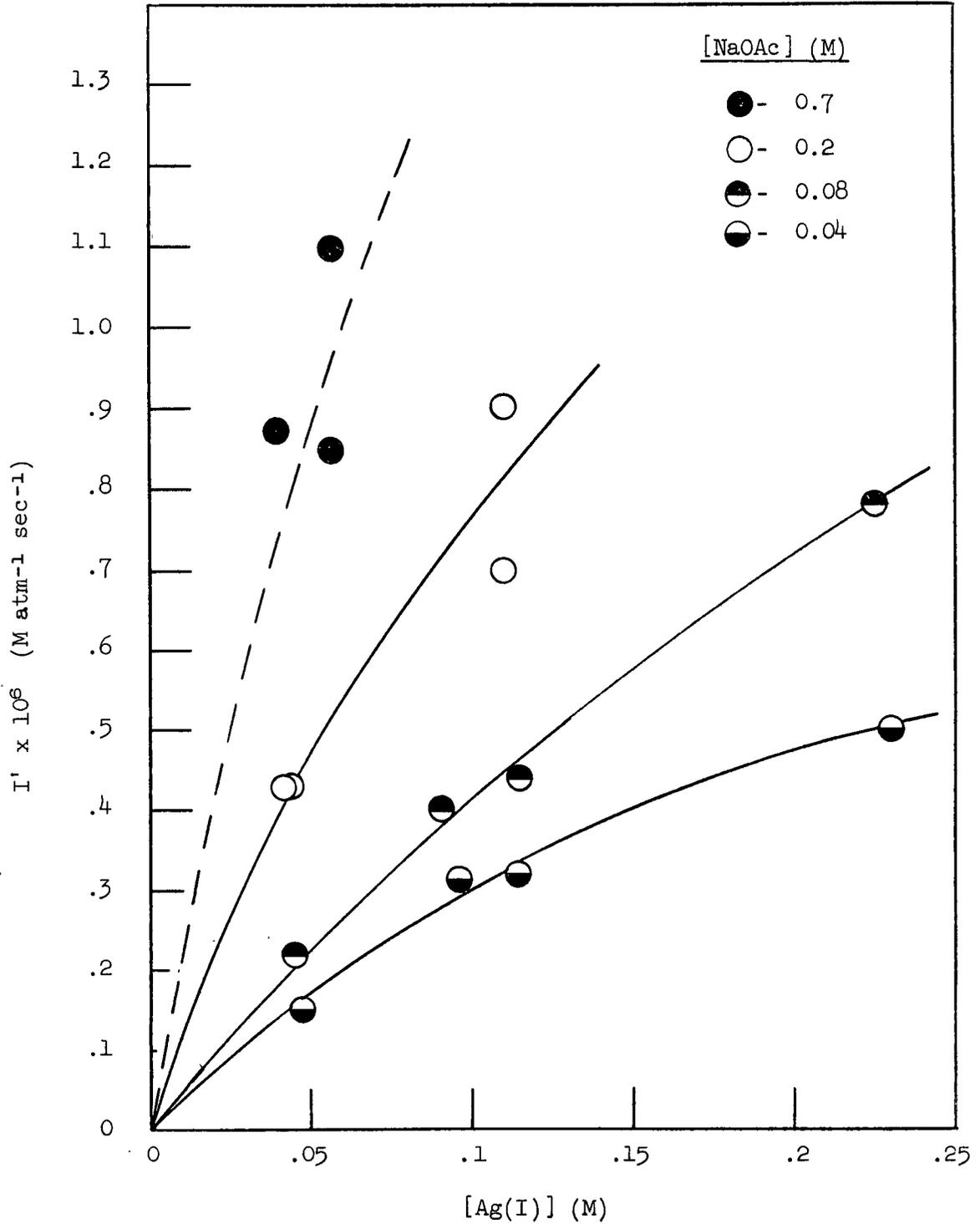


Figure 9. Dependence of Acid-Independent Reaction on  $[Ag(I)]$  at Various NaOAc Levels (90°C)

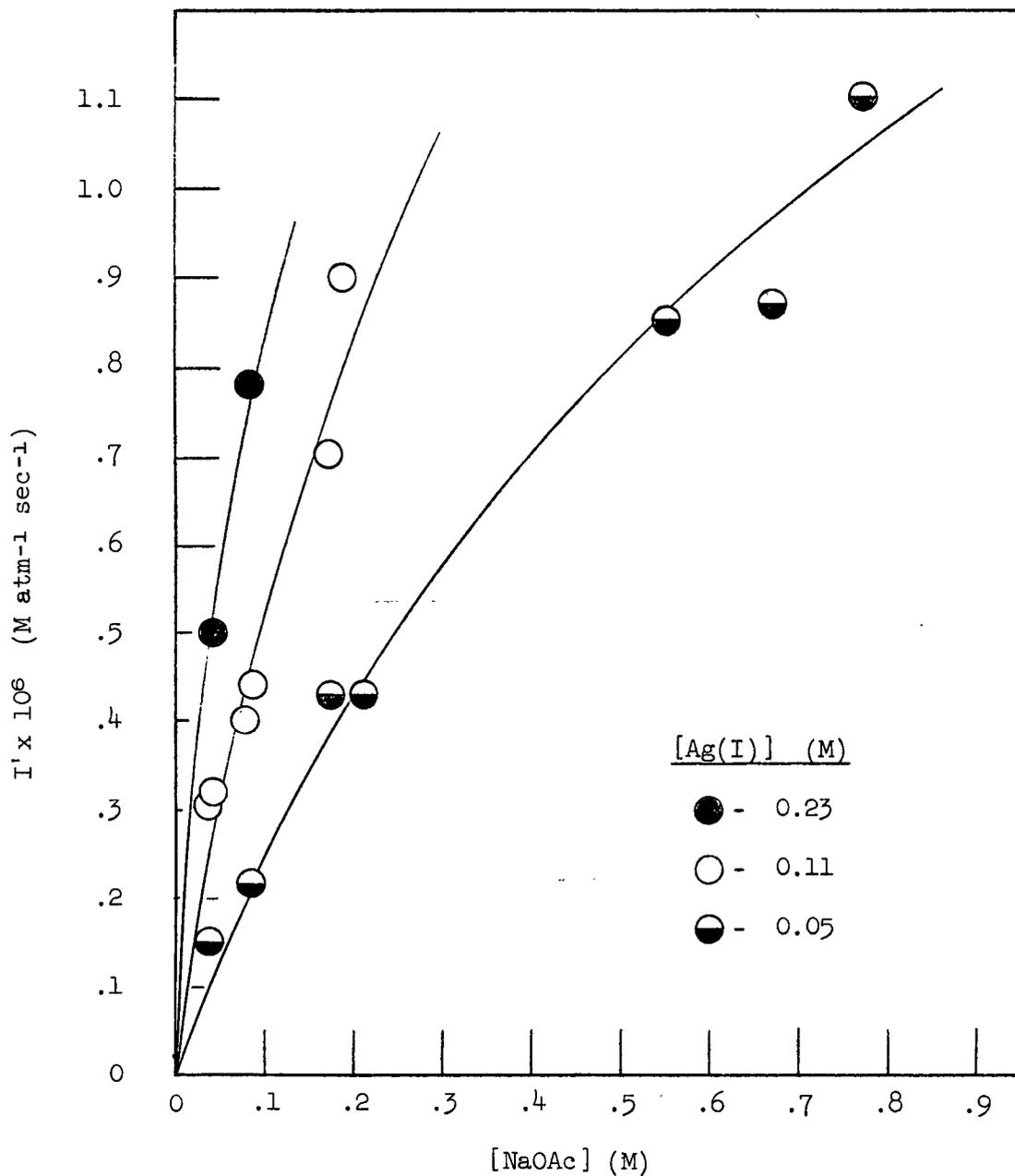


Figure 10. Dependence of Acid-Independent Reaction on  $[NaOAc]$  at Various  $Ag(I)$  Levels (90°C)

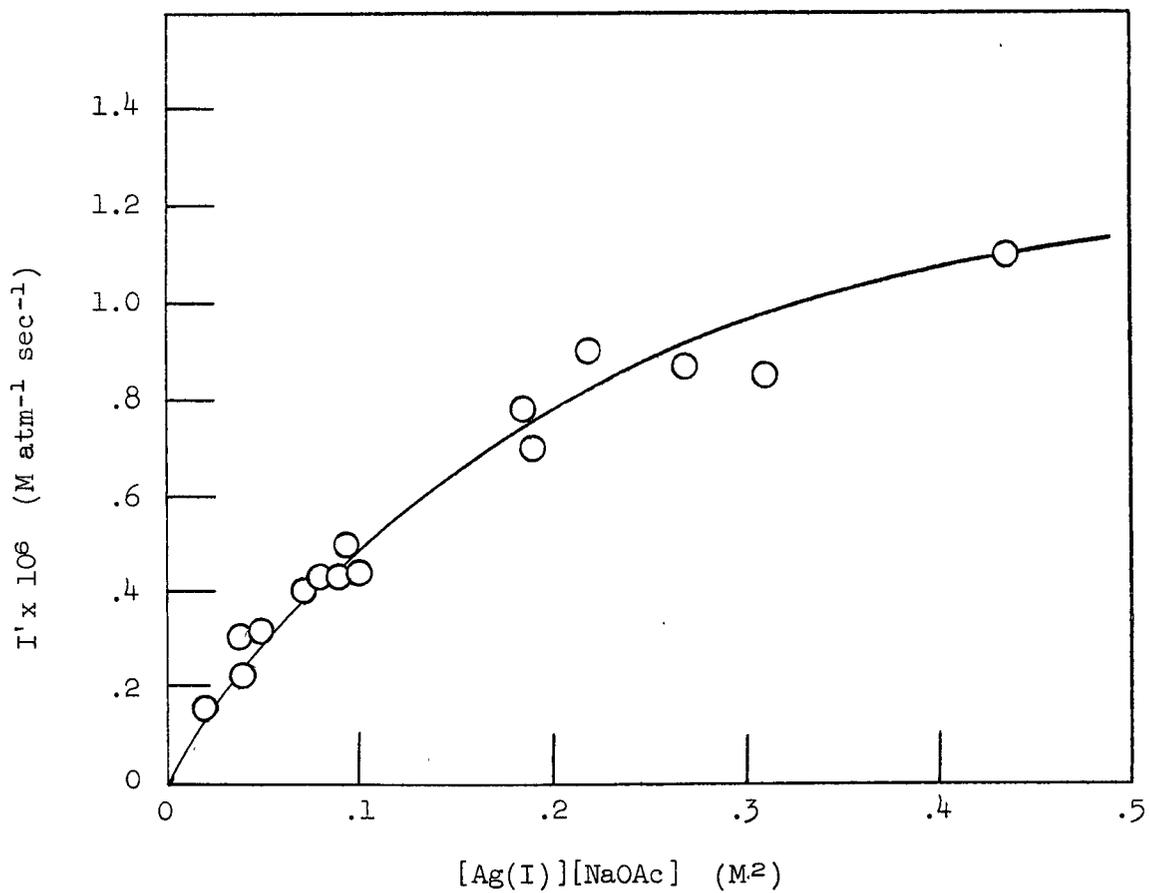
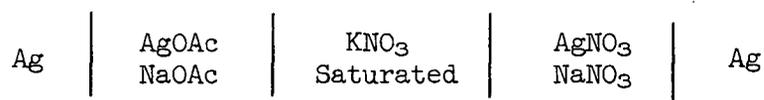


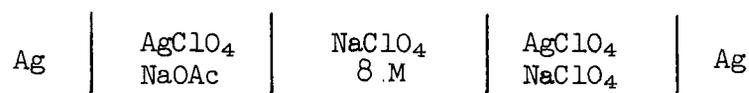
Figure 11. Dependence of Acid-Independent Reaction on  $[\text{Ag(I)}][\text{NaOAc}]$  ( $90^\circ\text{C}$ )

If the proposed form of the acid-independent contribution to the rate law is correct then a plot of  $[Ag(I)]/I'$  vs  $[OAc^-]^{-1}$  according to equation 10 should be linear with a slope of  $1/k_1'K_a$  and an intercept of  $1/k_1'$ . Figure 12 depicts such a plot where  $[OAc^-]$  has been approximated by  $[NaOAc]$ , which is a good estimate at high  $[NaOAc]$ . From Figure 12,  $k_1'$  has a value of about  $3 \times 10^{-5}$  atm<sup>-1</sup> sec<sup>-1</sup> while  $K_a$  has a value of about 2 M<sup>-1</sup>. If corrections are made for the amount of acetate effectively removed from solution through complexing with silver, assuming a value of 2 M<sup>-1</sup> for  $K_a$ , the intercept, and hence  $k_1'$ , remains essentially unchanged while the slope becomes flatter (i.e. the value for  $K_a$  increases). Using an iterative procedure of this type values of  $K_a$  between about two and five are obtained from the slope of  $[Ag(I)]/I'$  vs  $[OAc^-]^{-1}$  plots.

E.M.F. measurements using cells of the type:



have been made at room temperature (39) at ionic strength to about two. Using this reported data, assuming complete dissociation of  $AgNO_3$  and representing the concentration of  $Ag(I)$  present as silver-acetate complexes by  $[\overline{AgOAc}]$ , values for the ratio  $[\overline{AgOAc}]/[Ag^+][OAc^-] = K_a$  were found to lie between 2.8 and 3.4 M<sup>-1</sup> at ionic strengths between 0.1 and 0.9 increasing to 5.0 M<sup>-1</sup> at infinite dilution. To evaluate the temperature coefficient of  $K_a$ , further E.M.F. measurements were made during the present study at temperatures to 90°C and ionic strengths between 0.1 and 0.9 using cells of the type:



Complete details of these measurements and a summary of the results are given in Appendix C. Values of  $[\overline{AgOAc}]/[Ag^+][OAc^-] = K_a$  assuming complete dissociation of  $AgClO_4$  were found, within experimental error, to be effectively

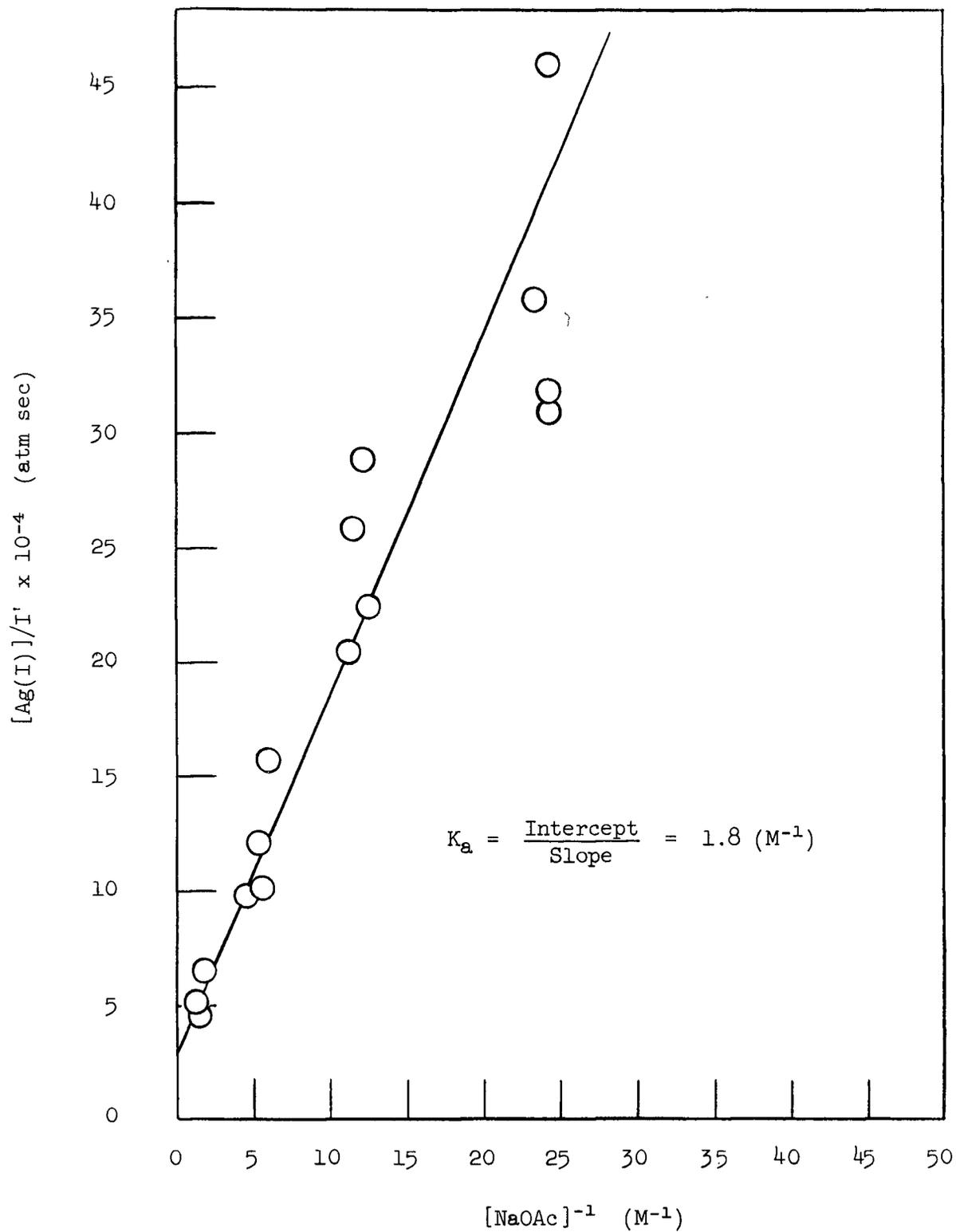


Figure 12. Dependence of Acid-Independent Reaction on  $[Ag(I)]$  and  $[NaOAc]$ ; plotted according to equation 10, assuming  $[OAc^-] = [NaOAc]$  ( $90^\circ C$ )

independent of temperature to 90°C and to lie between 3.0 and 4.4 M<sup>-1</sup> at ionic strengths of 0.1 to 0.9.

Using a value for  $K_a$  of 3.7 M<sup>-1</sup> to calculate the free acetate concentration  $[OAc^-]^*$  at 90°C, a plot of  $Ag(I)/I'$  vs  $[OAc^-]^{-1}$ , as in Figure 13, has an intercept equivalent to  $k_1' = 2.5 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$  and an average slope equivalent to  $K_a = 3.7 \text{ M}^{-1}$ . The slight curvature of the plot in Figure 13 might be due to a small systematic error in the estimation of  $[OAc^-]$ , or to higher order silver-acetate complexes (e.g.  $Ag(OAc^-)_2^-$ ) affecting the rate at high acetate levels. A plot of  $I'/[Ag^+]$  vs  $[OAc^-]$ , as in Figure 14, exhibits positive deviations from linearity with increasing  $[OAc^-]$  and thus supports the latter explanation for the curvature in Figure 13. The average slope of Figure 14 is equivalent to  $k_1'K_a$  and yields a value for  $k_1'$  of  $2.5 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$  assuming  $K_a = 3.7 \text{ M}^{-1}$ .

The dependence of the acid-independent reaction on silver-acetate complexing is also illustrated in Figure 15 where a plot of  $I'$  vs  $[\overline{AgOAc}]$  is linear, passing through the origin with a slope equivalent to  $k_1' = 2.5 \pm 0.6 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$ . The acid-independent contribution to the overall rate therefore has the form:

$$I' = k_1' [\overline{AgOAc}] \quad (7)$$

$$\text{or } I = k_1' P_{CO} [\overline{AgOAc}] \quad (11)$$

$$= k_1 [CO] [\overline{AgOAc}] \quad (12)$$

$$= k_1 K_a [CO] [Ag^+] [OAc^-] \quad (13)$$

where  $I$  = the acid-independent contribution to the overall rate of CO consumption (M sec<sup>-1</sup>)

$k_1$  = the apparent second-order specific rate constant for the acid-independent reaction (M<sup>-1</sup> sec<sup>-1</sup>)

---

\* For  $[OAc^-]$ ,  $[\overline{AgOAc}]$  and  $[Ag^+]$  values using  $K_a = 3.7 \text{ M}^{-1}$  see Table V, Section III-7.

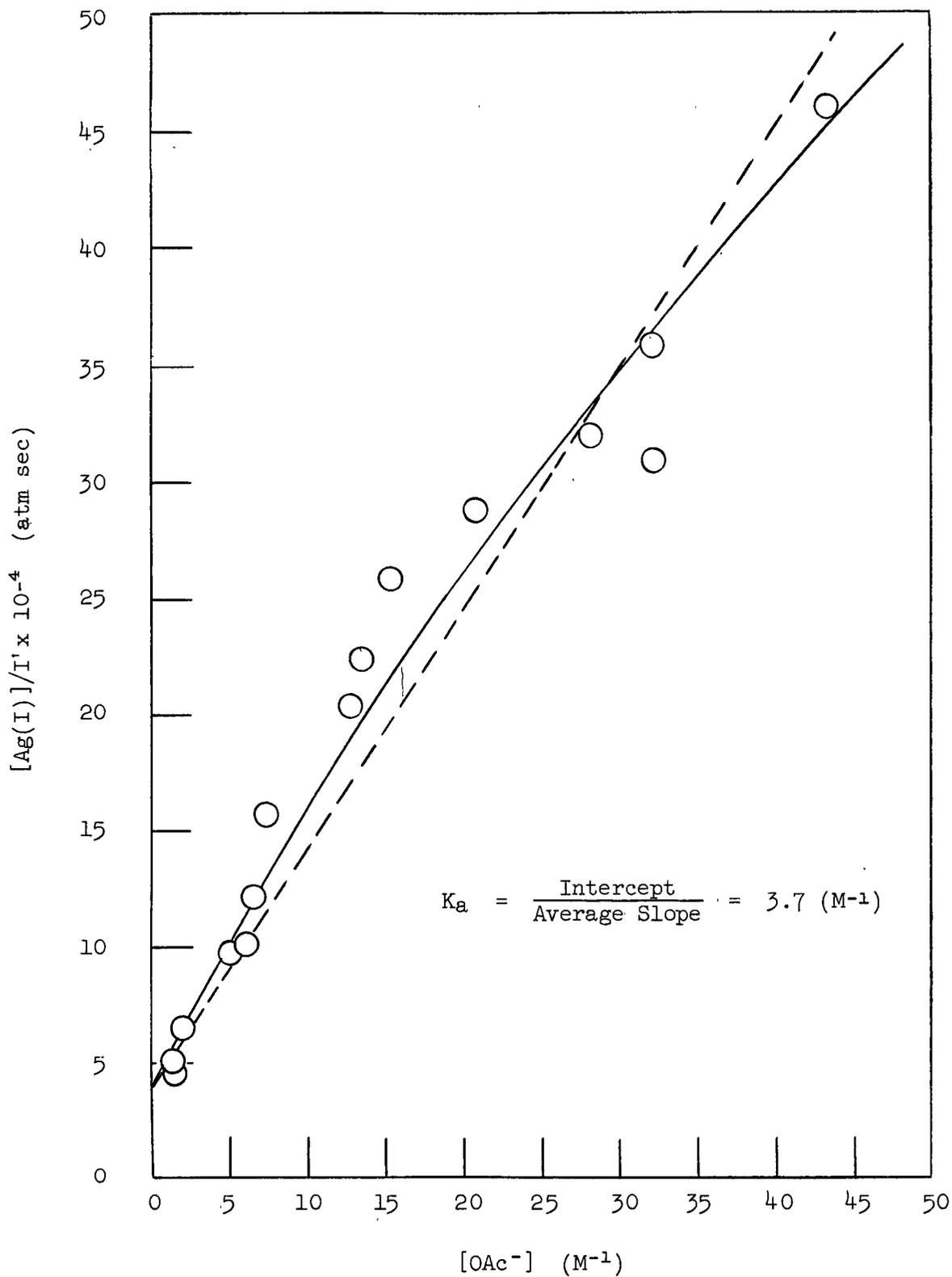


Figure 13. Dependence of Acid-Independent Reaction on  $[Ag(I)]$  and  $[OAc^-]$ ; plotted according to equation 10, assuming  $K_a = 3.7 M^{-1}$  ( $90^\circ C$ )

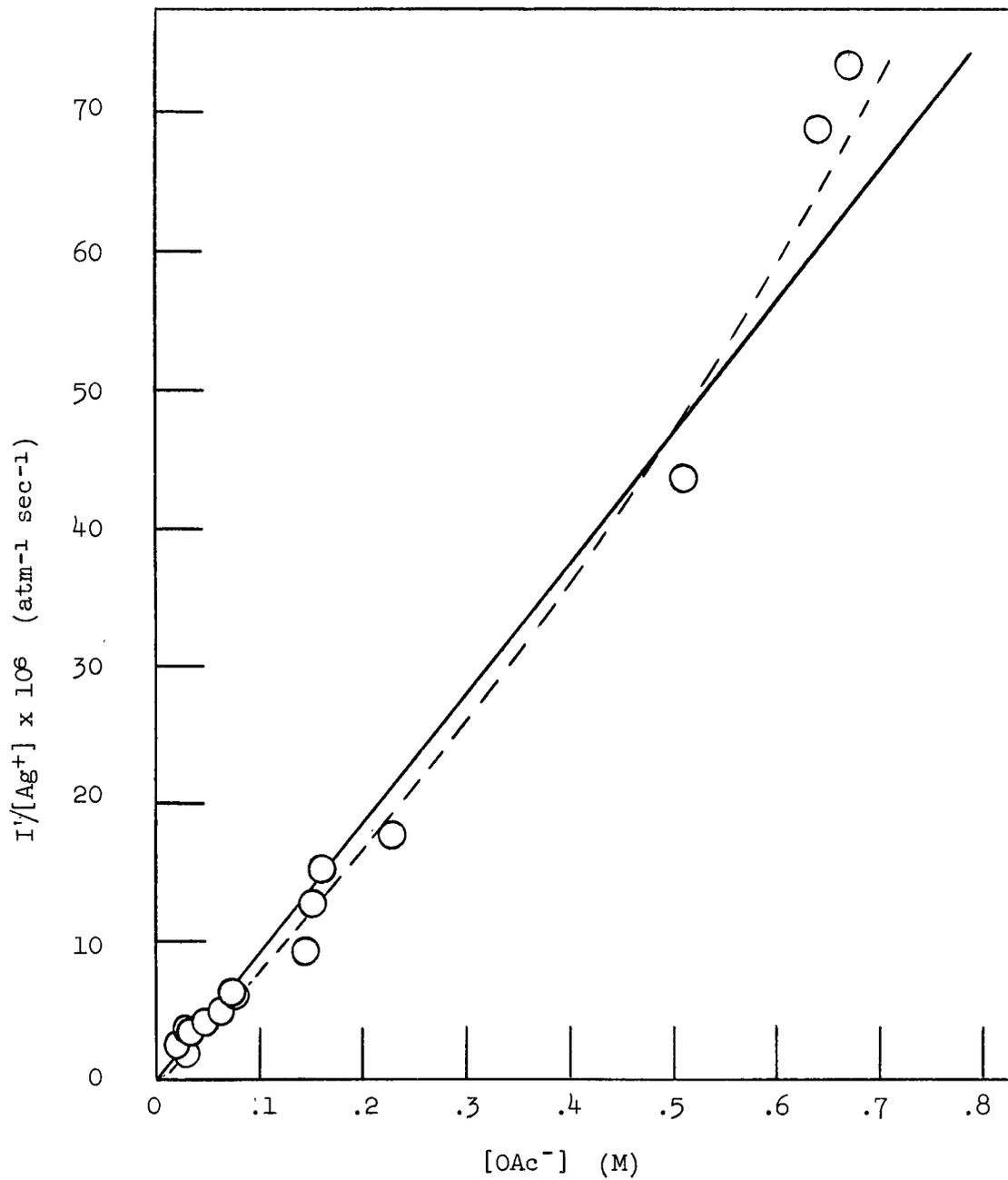


Figure 14. Dependence of Acid-Independent Reaction on  $[OAc^-]$  ( $90^\circ\text{C}$ )

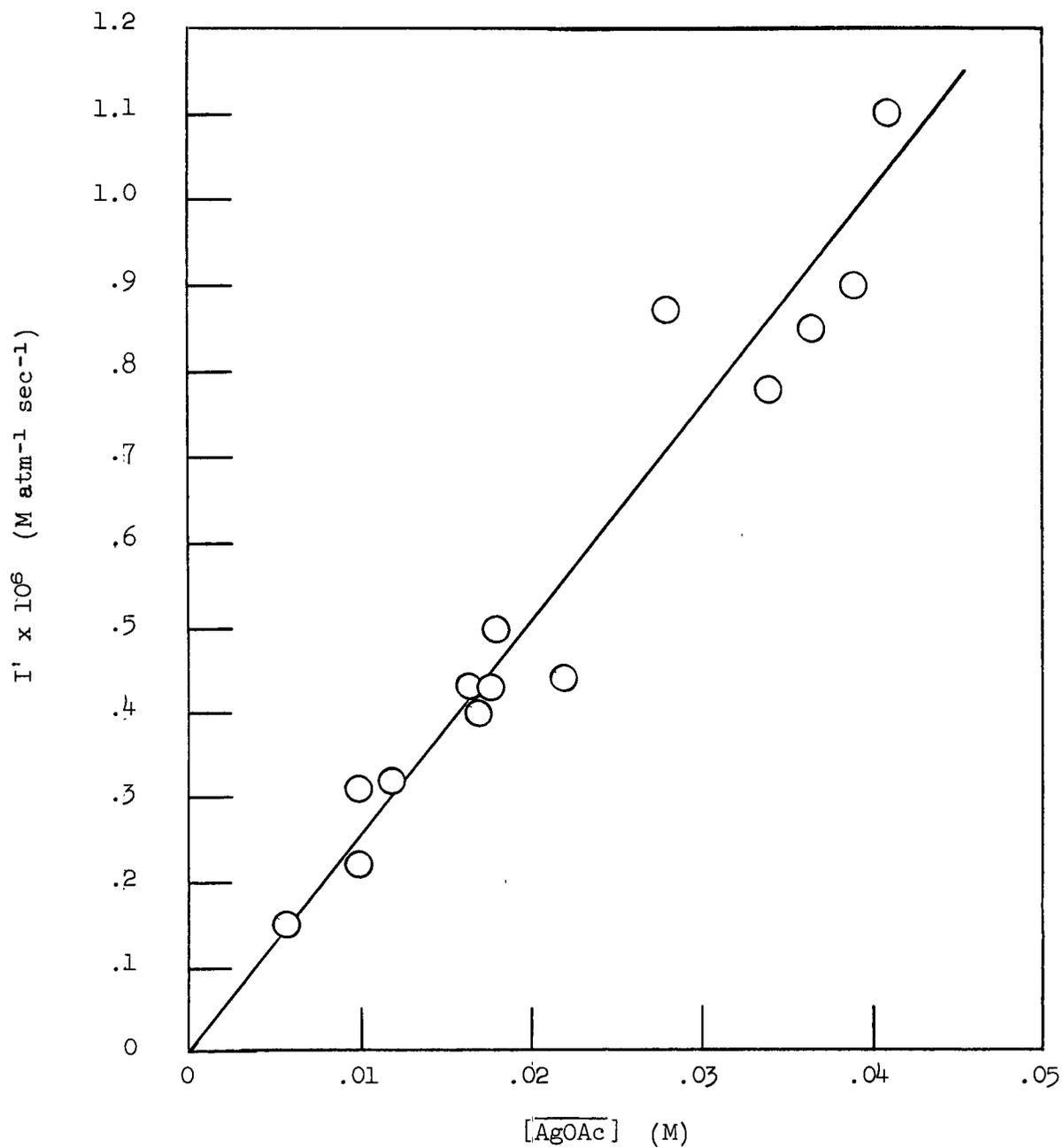


Figure 15. Dependence of Acid-Independent Reaction on  $[\text{AgOAc}]$  ( $90^\circ\text{C}$ )

Using a value for the solubility of CO in water of  $6.9 \times 10^{-4}$  M/atm at  $90^\circ\text{C}$  (see Appendix B) the experimental bimolecular rate constant  $k_1$  in equations 12 and 13 has a value of  $0.04 \pm .01 \text{ M}^{-1} \text{ sec}^{-1}$  at  $90^\circ\text{C}$ .

### III-7 Acid-Dependent Reaction

The variation of the acid-dependent reaction rate with initial  $[\text{Ag(I)}]$  and  $[\text{NaOAc}]$ , as summarized in Table IV (Section III-6), is depicted in Figures 16 and 17. The slope of the  $S'$  vs  $[\text{Ag(I)}]$  curves at constant  $[\text{NaOAc}]$  (Figure 16) increases with increasing  $[\text{Ag(I)}]$  and thus indicates that the acid-dependent reaction has a higher than first-order dependence on  $[\text{Ag}^+]$ .

Plots of  $S'$  vs  $[\text{NaOAc}]$  (Figure 17) and  $I'$  vs  $[\text{NaOAc}]$  (Figure 10) at constant  $[\text{Ag(I)}]$  have the same general shape in that the slopes decrease with increasing  $[\text{NaOAc}]$ . This indicates that  $S'$  has approximately the same dependence as  $I'$  on  $[\text{OAc}^-]$ , which has been shown to be first-order. It has also been demonstrated from  $R'$  vs  $[\text{HOAc}]^{-1}$  plots at constant degree of complexing that the acid-dependent reaction is inversely proportional to  $[\text{H}^+]$  or  $[\text{HOAc}]/[\text{OAc}^-]$ . The slopes,  $S'$ , of  $R'$  vs  $[\text{HOAc}]^{-1}$  plots therefore have a first-order  $[\text{OAc}^-]$  factor incorporated in them from the acid dependence.

A simple rate law, consistent with the shape of plots in Figures 16 and 17, to describe the acid-dependent reaction might involve a second-order dependence on uncomplexed silver and an inverse dependence on  $[\text{H}^+]$  or  $[\text{HOAc}]/[\text{OAc}^-]$ . In this case the slopes of  $R'$  vs  $[\text{HOAc}]^{-1}$  plots at constant degree of complexing would be given by:

$$S' = k_2' [\text{Ag}^+]^2 [\text{OAc}^-] \quad (14)$$

If equation 14 accurately represented the variation of  $S'$  then  $S'/[\text{Ag}^+]^2 [\text{OAc}^-]$  should be constant for all degrees of complexing. The experimental data, as

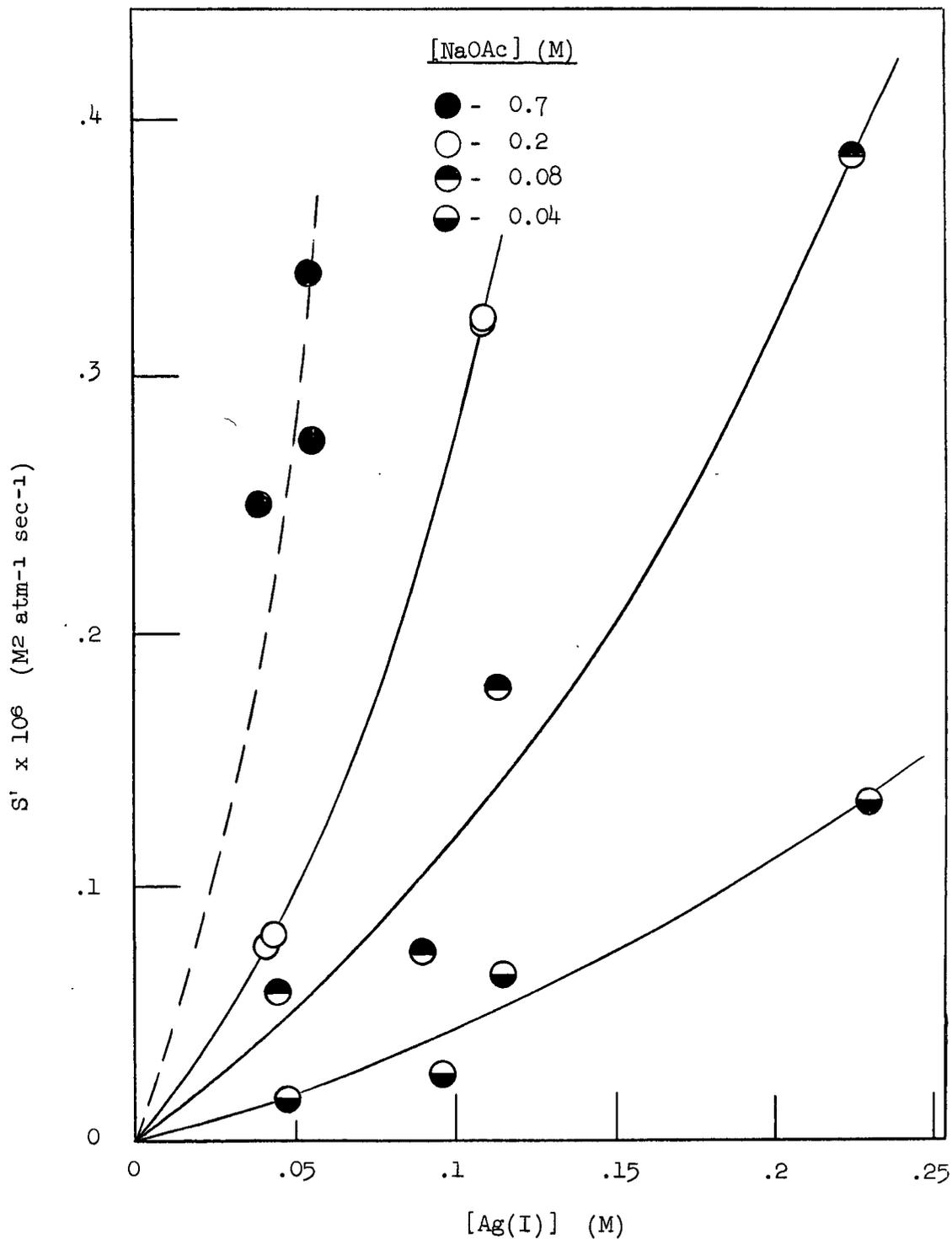


Figure 16. Dependence of Acid-Dependent Reaction on  $[\text{Ag(I)}]$  at Various NaOAc Levels ( $90^\circ\text{C}$ )

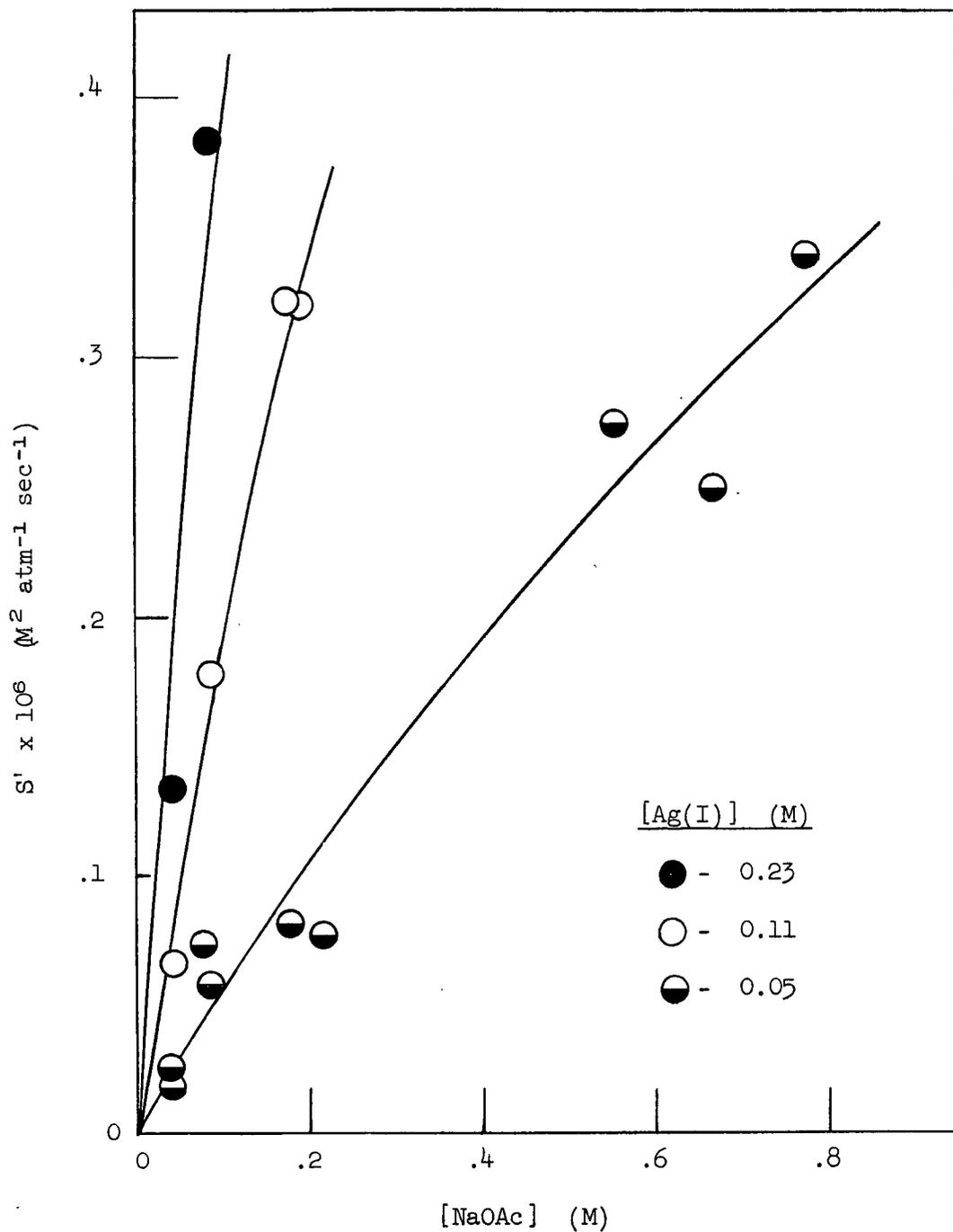


Figure 17. Dependence of Acid-Dependent Reaction on  $[\text{NaOAc}]$  at Various  $\text{Ag(I)}$  Levels ( $90^\circ\text{C}$ )

summarized in Table V, indicates that such is not the case, but rather  $S'/[Ag^+][OAc^-]$  increases with increasing  $[OAc^-]$  or decreasing  $[Ag^+]$ . This variation is taken as evidence for at least a two-term rate law to describe the acid-dependent reaction, e.g.:

$$S' = k_2' [Ag^+]^2 [OAc^-] + k_3'' [Ag^+]^2 [OAc^-]^2 \quad (15)$$

$$\text{or } S' = k_2' [Ag^+]^2 [OAc^-] + k_4'' [Ag^+] [OAc^-] \quad (16)$$

If either equation 15 or 16 represents the contribution to the rate for the acid-dependent term then plots of  $S'/[Ag^+]^2 [OAc^-]$  vs  $[OAc^-]$  or  $[Ag^+]^{-1}$  should be linear with intercepts of  $k_2'$  and slopes of  $k_3''$  or  $k_4''$  respectively. Figure 18 indicates that  $S'/[Ag^+]^2 [OAc^-]$  vs  $[OAc^-]$  is linear as predicted by equation 15 with a slope of  $3.2 \pm 0.8 \times 10^{-3} \text{ M}^{-2} \text{ atm}^{-1} \text{ sec}^{-1}$  and an intercept of  $7 \pm 7 \times 10^{-5} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$ .

Figure 19 shows that a plot of  $S'/[Ag^+]^2 [OAc^-]$  vs  $[Ag^+]^{-1}$  is not linear, except perhaps at low  $[Ag^+]^{-1}$  values, indicating that equation 16 is inadequate to describe the experimental observations over the entire concentration range investigated. Increasing positive deviations at higher  $[Ag^+]^{-1}$  values, which also correspond to higher  $[OAc^-]$ , might be evidence for greater activity of  $Ag(OAc)_2^-$  relative to  $AgOAc^*$ . Subsequent measurements presented in Sections III-8 and III-9, however, favour equation 15 to describe the acid-dependent contribution to the rate law. Thus the rate law for the acid-dependent reaction can be expressed as:

$$D' = k_2' [Ag^+]^2 \frac{[OAc^-]}{[HOAc]} + k_3'' [Ag^+]^2 [OAc^-] \frac{[OAc^-]}{[HOAc]} \quad (17)$$

$$= k_2' [Ag^+]^2 \frac{[OAc^-]}{[HOAc]} + k_3' [Ag^+] \frac{[AgOAc]}{[HOAc]} \frac{[OAc^-]}{[HOAc]} \quad (18)$$

---

\* Based on available stability constant data at room temperature (38), the ratio of  $AgOAc$  to  $Ag(OAc)_2^-$  is about 5:1 at 0.2 M NaOAc.

TABLE V

Summary of the Dependence of S' on  $[Ag^+]$ \* at 90°C

Series** Code	$S' \times 10^6$ $M^2 a^{-1} s^{-1}$	$[Ag(I)]$ M	$[NaOAc]$ M	$[\overline{AgOAc}]$ M	$[Ag^+]$ M	$[OAc^-]$ M	$[Ag^+]^{-1}$ $M^{-1}$	$\frac{S' \times 10^4}{[Ag^+]^2 [OAc^-]}$ $M^{-1} a^{-1} s^{-1}$
B	.026	.096	.041	.010	.086	.031	11.6	1.1
H	.133	.230	.041	.018	.212	.023	4.7	1.3
D	.066	.115	.043	.011	.103	.031	9.7	2.1
J	.384	.225	.082	.034	.191	.048	5.3	2.2
E	.074	.090	.080	.017	.063	.073	15.9	2.6
A	.017	.048	.041	.0056	.042	.035	23.6	2.7
I	.178	.114	.087	.022	.092	.065	10.9	3.3
L	.320	.110	.190	.039	.071	.151	14.1	4.3
K	.322	.110	.173	.036	.073	.136	13.7	4.4
C	.058	.045	.089	.010	.035	.078	28.6	6.1
F	.081	.044	.178	.016	.027	.161	36.4	7.0
G	.077	.042	.215	.017	.024	.197	41.2	7.0
N	.275	.056	.550	.036	.019	.513	51.3	14.8
O	.340	.056	.780	.041	.015	.739	66.7	20.4
M	.249	.040	.670	.028	.012	.642	84.4	27.4

\* Values of  $[Ag^+]$  and  $[\overline{AgOAc}]$  were estimated using  $K_a = 3.7 M^{-1}$ 

\*\* See Appendix D for Series Code references

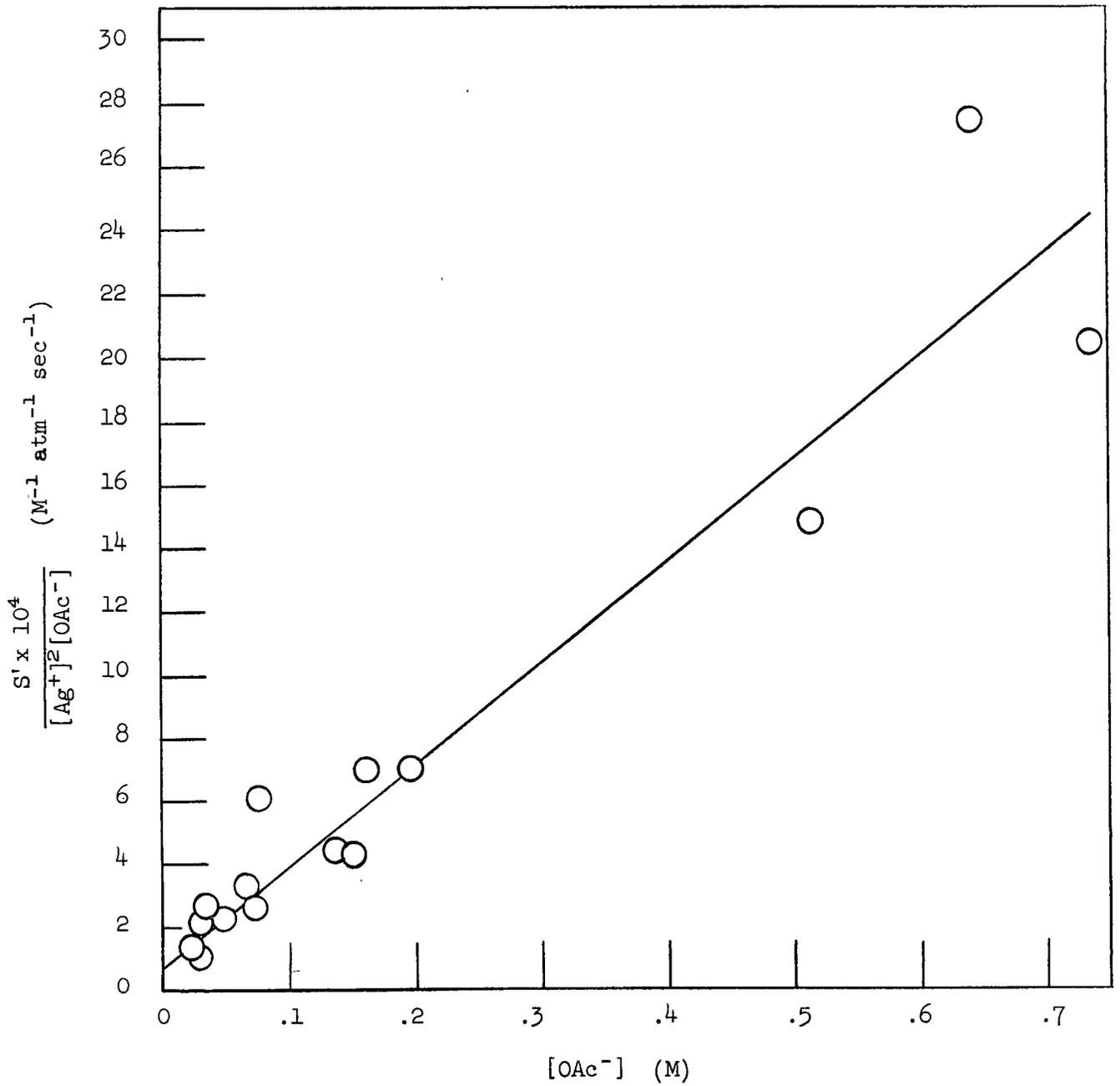


Figure 18. Dependence of Acid-Dependent Reaction on Acetate Complexing; plotted according to equation 15 (90°C)

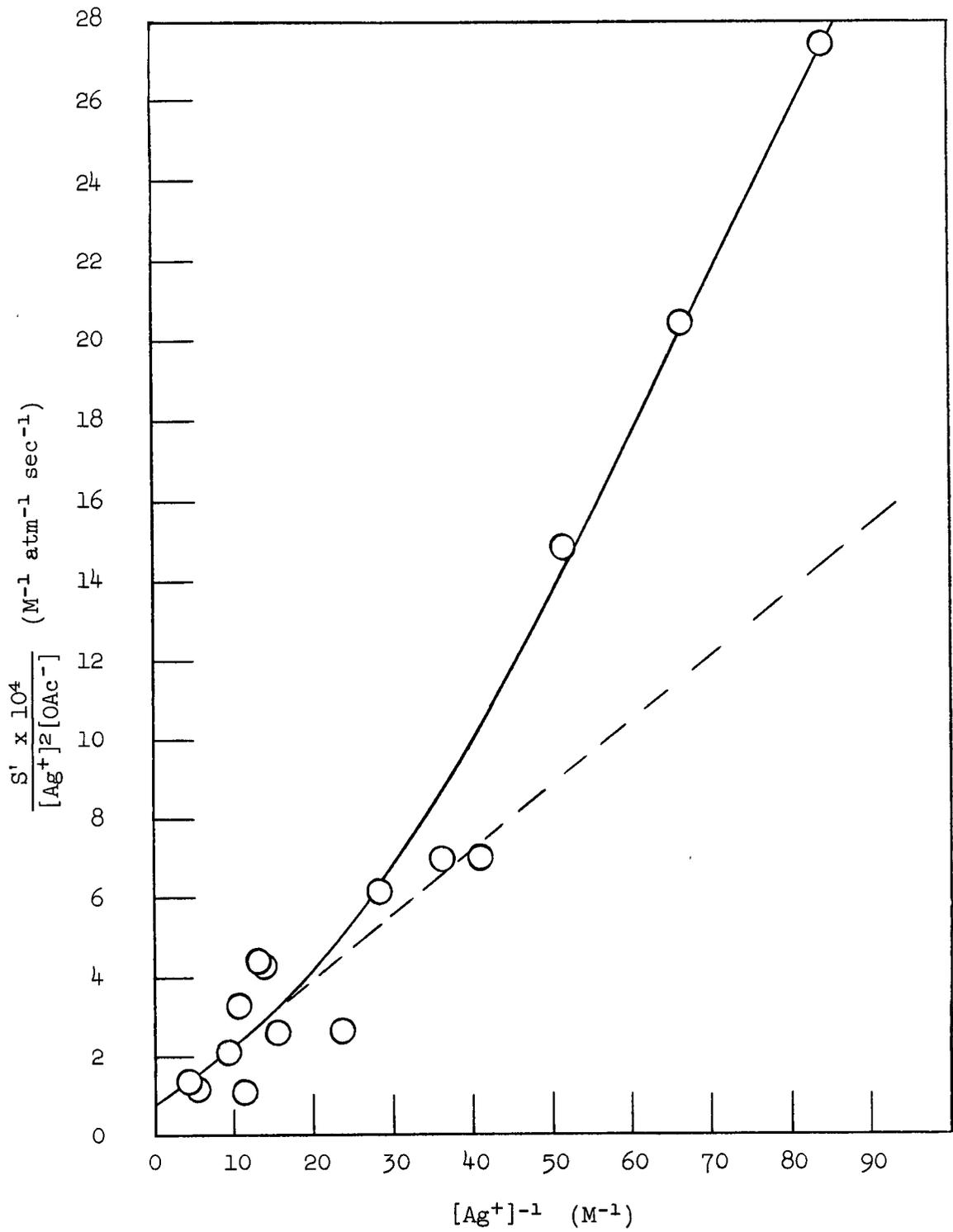


Figure 19. Dependence of Acid-Dependent Reaction on Acetate Complexing; plotted according to equation 16 (90°C)

The overall rate law including both the acid-independent and the acid-dependent reactions then becomes:

$$R' = k_1' [\overline{\text{AgOAc}}] + k_2' [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3' [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (19)$$

$$R = k_1 [\text{CO}] [\overline{\text{AgOAc}}] + k_2 [\text{CO}] [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3 [\text{CO}] [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (20)$$

From Figure 18,  $k_2' = 7 \pm 7 \times 10^{-5} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$  and  $k_3' = k_3''/K_a = 9.0 \pm 2.1 \times 10^{-4} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$ . Using a value of  $6.9 \times 10^{-4} \text{ M/atm}$  for the solubility of CO in water (see Appendix B) yields values for  $k_2$  and  $k_3$  in equation 20 of  $0.1 \pm 0.1 \text{ M}^{-2} \text{ sec}^{-1}$  and  $1.3 \pm 0.3 \text{ M}^{-2} \text{ sec}^{-1}$  respectively, at  $90^\circ\text{C}$ . From Section III-5  $k_1$  has a value of  $0.04 \pm .01 \text{ M}^{-1} \text{ sec}^{-1}$ .

### III-8 Acetate-Independent Reaction

In equation 19 the  $k_2'$ -term is acetate-independent since  $[\text{HOAc}]/[\text{OAc}^-]$  is simply a measure of  $[\text{H}^+]$ . To verify the form of the acetate-independent contribution to the rate law several series of experiments were conducted at various low NaOAc levels using constant  $[\text{Ag(I)}]$  and HOAc/NaOAc ratios. Extrapolation of each series to zero  $[\text{NaOAc}]$  yields a measure of the reduction rate in the absence of acetate complexing. Several plots of this type are depicted in Figure 20.

Although the total  $[\text{Ag(I)}]$  and HOAc/NaOAc ratio were held constant during each series,  $[\text{Ag}^+]$  and  $[\text{HOAc}]/[\text{OAc}^-]$  (or  $[\text{H}^+]$ ) varied with each experiment due to differing degrees of silver-acetate complexing at the various acetate levels used. To minimize these effects plots of  $R' [\text{HOAc}]/[\overline{\text{AgOAc}}]$  vs  $[\text{OAc}^-]$  calculated using  $K_a = 3.7 \text{ M}^{-1}$  were extrapolated to zero  $[\text{OAc}^-]$  as shown in Figure 21. Rearrangement of equation 19 according to equation 21,

$$R' \frac{[\text{HOAc}]}{[\overline{\text{AgOAc}}]} = \left( k_1' \frac{[\text{HOAc}]}{[\text{OAc}^-]} + k_3' [\text{Ag}^+] \right) [\text{OAc}^-] + \frac{k_2'}{K_a} [\text{Ag}^+] \quad (21)$$

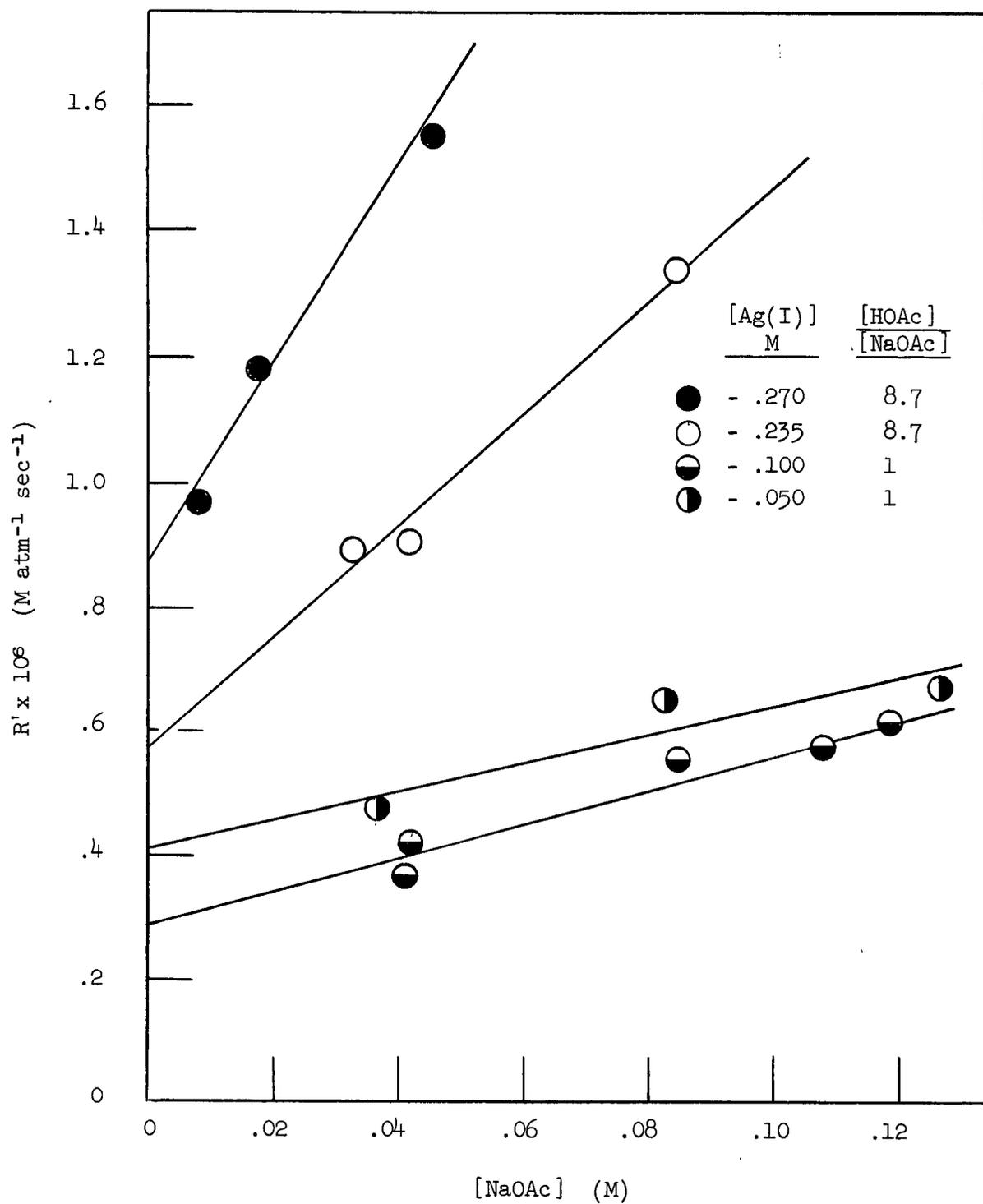


Figure 20. Dependence of Rate on [NaOAc] at Constant [Ag(I)] and [HOAc]/[NaOAc] (90°C)

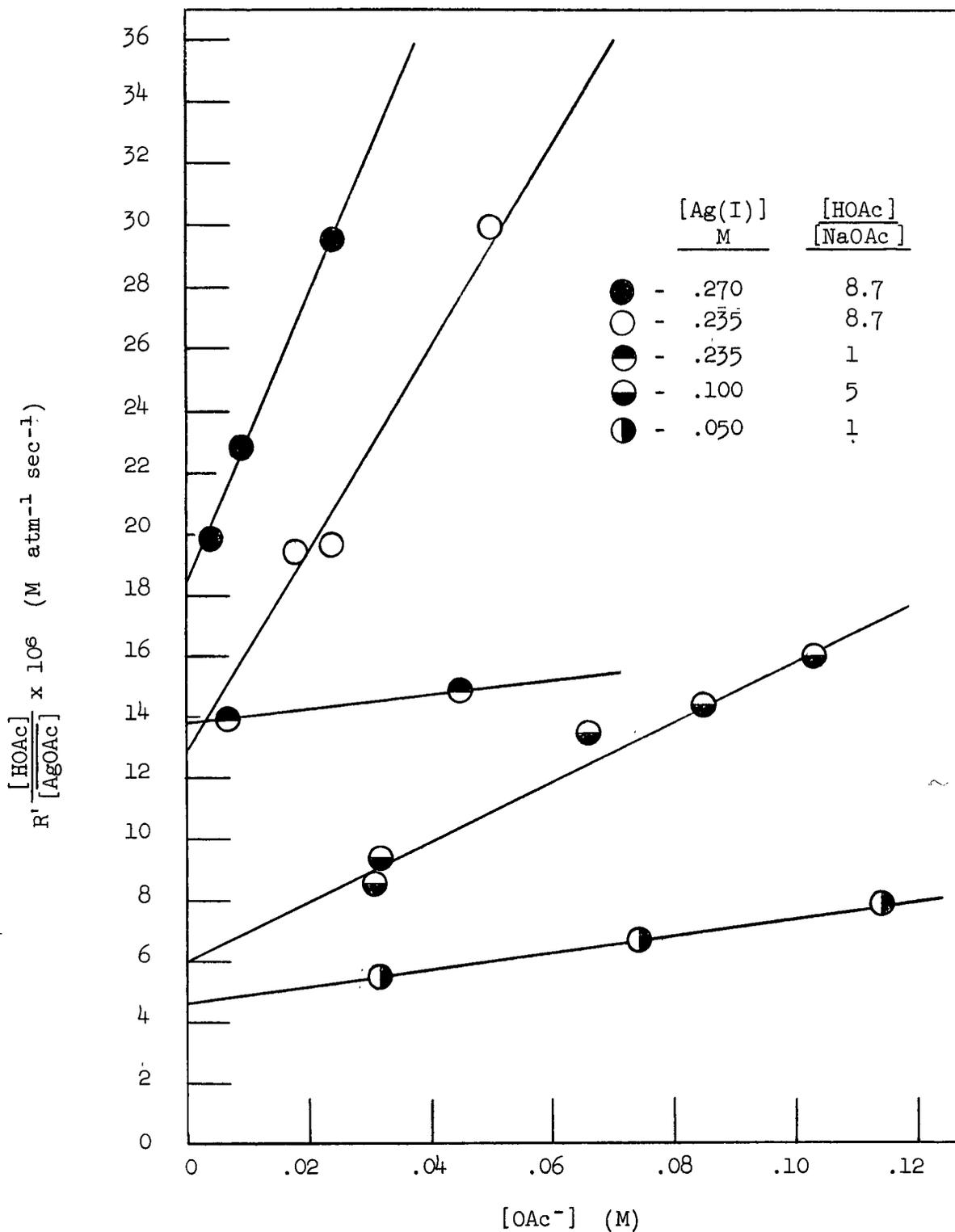


Figure 21. Dependence of  $R' \frac{[\text{HOAc}]}{[\text{AgOAc}]}$  on  $[\text{OAc}^-]$  at Constant  $[\text{Ag(I)}]$  and  $[\text{HOAc}]/[\text{NaOAc}]$ ; plotted according to equation 21 (90°C)

indicates that the intercepts of plots of this latter type are equivalent to  $k_2' [Ag^+]/K_a$  while the slopes are equivalent to average values of  $k_1' [HOAc]/[OAc^-] + k_3' [Ag^+]$ . Table VI summarizes the intercepts,  $(R' [HOAc]/[AgOAc])_0$ , obtained from ten  $R' [HOAc]/[\overline{AgOAc}]$  vs  $[OAc^-]$  plots including those shown in Figure 21. Since the intercepts are equivalent to  $k_2' [Ag^+]/K_a$  a plot of  $(R' [HOAc]/[\overline{AgOAc}])_0$  vs  $[Ag^+]$  should be linear passing through the origin with a slope of  $k_2'/K_a$ . Such a plot, as depicted in Figure 22, indicates that the data, although exhibiting a high degree of scatter (due presumably to the inherent difficulty of measuring slow rates by the pressure-drop method), is consistent with a linear relationship having a slope of  $8 \pm 4 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$ . Thus the acetate-independent contribution to the overall rate law can be expressed as:

$$R_{O'} = k_2' \frac{[Ag^+]^2 [OAc^-]}{[HOAc]} = k_2' K_i \frac{[Ag^+]^2}{[H^+]} \quad (22)$$

$$\text{or } R_O = k_2 \frac{[CO][Ag^+]^2 [OAc^-]}{[HOAc]} = k_2 K_i \frac{[CO][Ag^+]^2}{[H^+]} \quad (23)$$

where  $K_i$  is the ionization constant of acetic acid.

From the slope of Figure 22, using a value of  $3.7 \text{ M}^{-1}$  for  $K_a$ ,  $k_2' = 30 \pm 15 \times 10^{-5} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$ , and using a value of  $6.9 \times 10^{-4} \text{ M/atm}$  for  $\alpha_{CO}$ ,  $k_2 = 0.4 \pm 0.2 \text{ M}^{-2} \text{ sec}^{-1}$  at  $90^\circ\text{C}$ . In Section III-7,  $k_2'$  and  $k_2$  were estimated to be  $7 \pm 7 \times 10^{-5} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$  and  $0.1 \pm 0.1 \text{ M}^{-2} \text{ sec}^{-1}$  respectively.

### III-9 Reduction of Unbuffered Silver Perchlorate

A more direct estimation of the acetate-independent contribution to the overall rate can be made from rate measurements in unbuffered  $AgClO_4$  solutions. The perchlorate ion is among the weakest complexing ligands for metal ions in aqueous solution (40). Thus in a solution of  $AgClO_4$  in the

TABLE VI

Summary of Acetate-Independent Rates  
 At Various HOAc/NaOAc ratios and Ag(I) Levels at 90°C

Series* Code	No of Expts	[Ag(I)] M	$\frac{[\text{HOAc}]}{[\text{NaOAc}]}$	$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0$ M a <sup>-1</sup> s <sup>-1</sup>
				x 10 <sup>6</sup>
P	6	.050	1	4.6
Q	3	.100	1	6.8
R	2	.123	1	9.6
S	2	.235	1	13.7
T	5	.100	5	6.0
U	2	.064	8.7	4.4
V	2	.130	8.7	18.0
W	2	.163	8.7	19.4
X	3	.233	8.7	12.8
Y	4	.270	8.7	18.4

\* See Appendix D for Series Code references

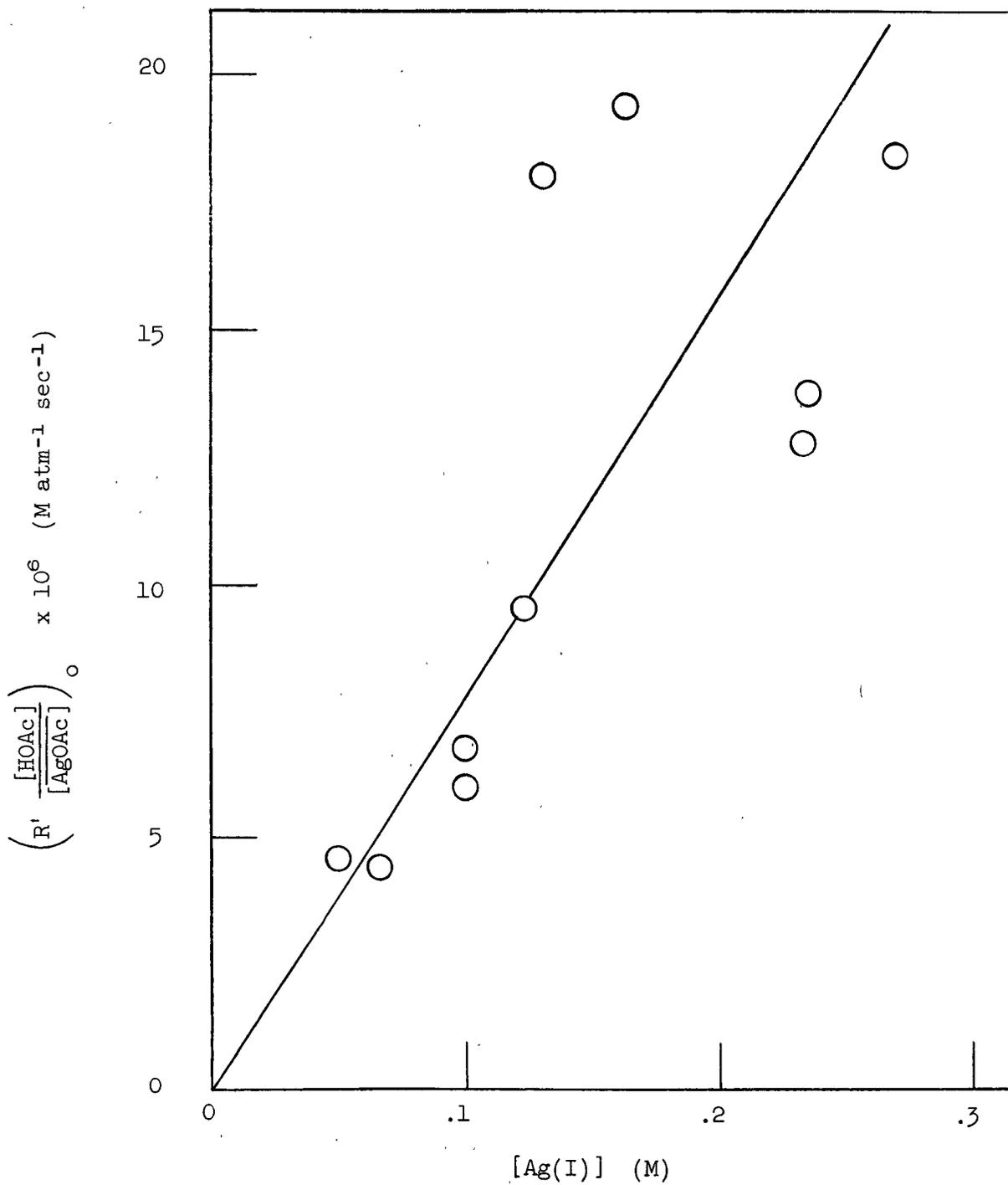
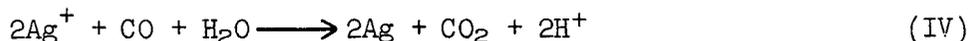


Figure 22. Dependence of Acetate-Independent Reaction on  $[\text{Ag(I)}]$  ( $90^\circ\text{C}$ )

absence of other complexing agents. the silver can be considered to exist exclusively as the aquo-complex. Unfortunately the rate of CO consumption in such a system is too slow to be easily measured using the pressure-drop method. By measuring the pH of periodic liquid samples, however, the CO consumption can be calculated using the stoichiometry represented by reaction IV (i.e.  $-2d[CO]/dt = d[H^+]/dt$ ):



Four such experiments were conducted at varying  $[AgClO_4]$  using constant CO pressures of about 53 atm at 90°C. The stoichiometry between the consumption of  $Ag^+$  and the production of  $H^+$  as shown in Table VII is consistent with reaction IV.

In Section III-8 it was shown that the acetate-independent reaction can be represented by a rate law of the form:

$$R_0' = k_2'K_1[Ag^+]^2/[H^+] \quad (22)$$

The duration of each experiment reported in the present section was equivalent to about 15% reduction and hence  $[Ag^+]$  as well as the CO pressure remained essentially constant during each experiment. Equation 22 is thus equivalent to:

$$d[H^+]/dt = -2d[CO]/dt = k_2'''/[H^+] \quad (23)$$

The effect of CO pressure was not investigated and is assumed to be first-order. Since  $[Ag^+]$  remained constant during each experiment it is not

---

\* Concentrations of  $H^+$  were calculated from pH measurements made with a Beckman pH-meter (Model G) calibrated against mixtures of standard  $HClO_4$  and  $AgClO_4$  solutions using glass and saturated calomel electrodes with an additional saturated potassium chloride and filter paper salt bridge.

TABLE VII

Stoichiometry of Unbuffered CO - Silver Perchlorate Reaction

at 90°C and 53 atm CO

Expt No	[AgClO <sub>4</sub> ] (M)			[H <sup>+</sup> ] (M)			$\frac{\Delta[\text{Ag}^+]}{\Delta[\text{H}^+]}$
	Initial	Final	Consumed	Initial	Final	Produced	
262	.0530	.0458	.0072	$7 \times 10^{-6}$	.0081	.0081	0.9
260	.1040	.0897	.0143	$1 \times 10^{-5}$	.0135	.0135	1.1
261	.211	.179	.032	$3 \times 10^{-5}$	.0339	.0339	0.9
263	1.060	.850	.210	$1 \times 10^{-4}$	.204	.204	1.0

necessary to assume a second-order  $[Ag^+]$  dependence in unbuffered  $AgClO_4$  solution. The rate constant  $k_2'''$  in equation 23 is thus equivalent to:

$$k_2''' = 2k_2'K_1[Ag^+]^n P_{CO} \quad (24)$$

Integration of equation 23 from zero to  $t$  yields:

$$[H^+]^2 - [H^+]_0^2 = 2k_2'''t \quad (25)$$

But rapid initial reaction quickly makes  $[H^+]_0$  negligibly small with respect to  $[H^+]$ . Taking logarithms of equation 25 gives:

$$\log [H^+] = 0.5 \log t + \log k_2''' \quad (26)$$

$$pH = -0.5 \log t - \log k_2''' \quad (27)$$

Plots of pH vs  $\log t$  at constant  $[Ag^+]$  and  $P_{CO}$  should be linear with slopes of  $-0.5$ . Figure 23 shows that this prediction is essentially correct with slight deviations from linearity being explained by the decrease in  $[Ag^+]$  and the simultaneous formation of small amounts of  $CO_2$  during each experiment.

Values of  $k_2'''$  can be obtained from Figure 23 using the differential logarithmic form of equation 23:

$$k_2''' = \frac{[H^+]^2}{t} \frac{d(\log[H^+])}{d(\log t)} \quad (28)$$

A summary of  $k_2'''$  values obtained in this manner, assuming  $d(\log[H^+])/d(\log t) = 0.5$ , is given in Table VIII.

The apparent dependence of  $k_2'''$  on  $[Ag^+]$  can also be found from Figure 23 by plotting pH values, obtained at equal times for each of the four experiments, against  $\log [Ag^+]$ . That the slope of such a plot should be  $-0.5$  times the apparent order of the  $[Ag^+]$  dependence follows from equations 28 and 24 where at constant  $t$ ,  $P_{CO}$ , and  $d(\log[H^+])/d(\log t)$ :

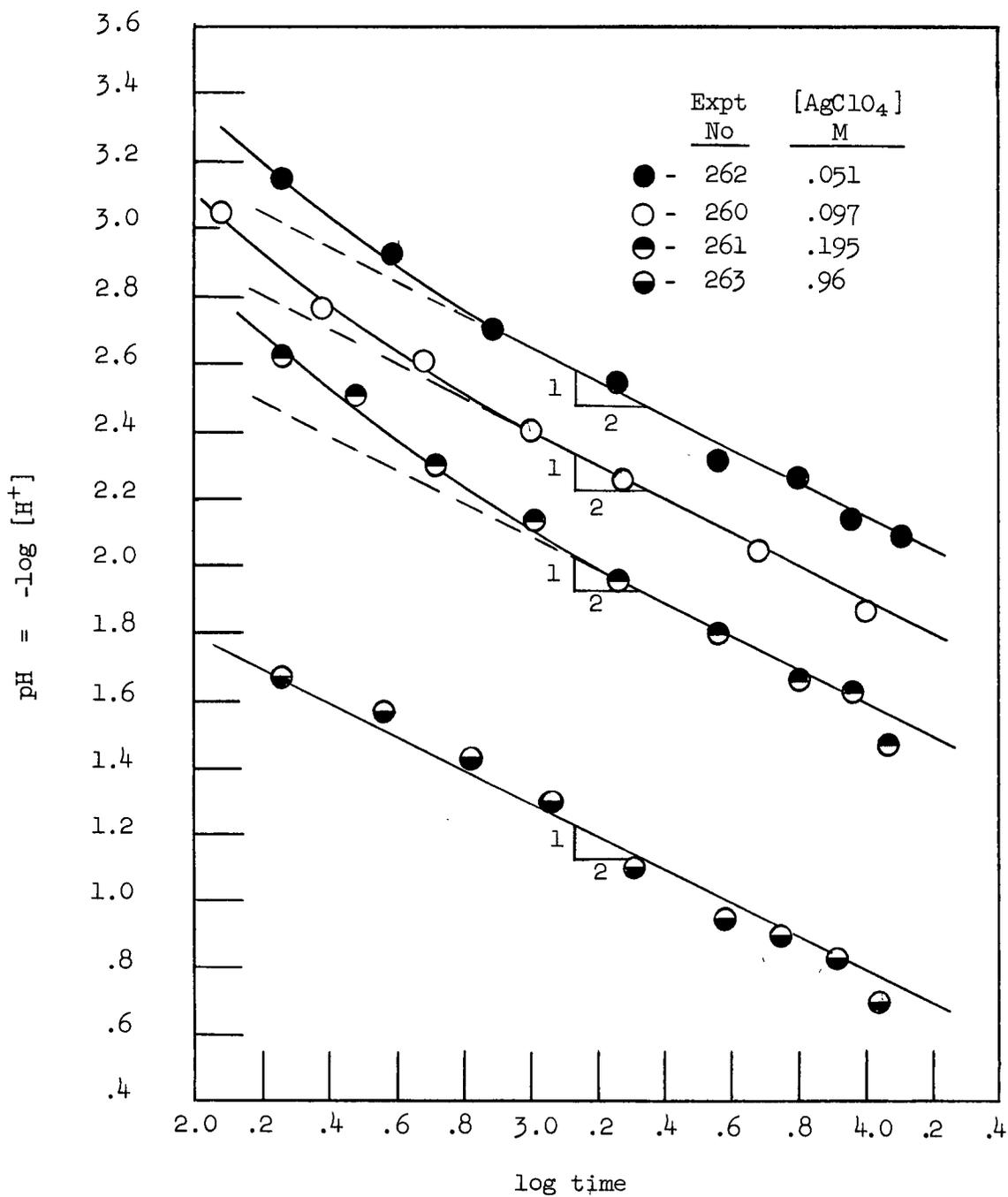


Figure 23. Reduction Rate of AgClO<sub>4</sub> in Unbuffered Solution; plotted according to equation 27 (53 atm; 90°C)

TABLE VIII

Summary of Experimental Rate Constants  
in Unbuffered Silver Perchlorate Solutions at 90°C and 53 atm CO

[Ag <sup>+</sup> ] M	log [Ag <sup>+</sup> ]	t = 1000 sec				t = 10,000 sec				Mean k <sub>2</sub> <sup>''</sup> a <sup>-1</sup> s <sup>-1</sup>
		pH	[H <sup>+</sup> ] M	k <sub>2</sub> <sup>'''*</sup> M <sup>2</sup> s <sup>-1</sup>	k <sub>2</sub> <sup>''**</sup> a <sup>-1</sup> s <sup>-1</sup>	pH	[H <sup>+</sup> ] M	k <sub>2</sub> <sup>'''*</sup> M <sup>2</sup> s <sup>-1</sup>	k <sub>2</sub> <sup>''**</sup> a <sup>-1</sup> s <sup>-1</sup>	
			x 10 <sup>3</sup>		x 10 <sup>9</sup>		x 10 <sup>3</sup>		x 10 <sup>9</sup>	x 10 <sup>9</sup>
0.051	2.71	2.65	2.24	2.6 x 10 <sup>-9</sup>	9.5	2.14	7.25	2.6 x 10 <sup>-9</sup>	9.5	9.5
0.097	2.99	2.40	3.98	7.9 x 10 <sup>-9</sup>	7.9	1.88	13.2	8.7 x 10 <sup>-9</sup>	8.7	8.3
0.195	1.24	2.11	7.76	3.0 x 10 <sup>-8</sup>	7.5	1.55	28.2	4.0 x 10 <sup>-8</sup>	9.9	8.7
0.96	1.98	1.33	46.8	1.1 x 10 <sup>-6</sup>	11.3	0.79	162.	1.3 x 10 <sup>-6</sup>	13.3	12.3

\*  $k_2''' = \frac{[H^+]^2}{t} \frac{d(\log[H^+])}{d(\log t)}$  according to equation 28

\*\*  $k_2'' = 0.5 k_2''' / [Ag^+]^2 P_{CO}$  according to equation 34

$$k_2''' = \text{constant} \times [\text{H}^+]^2 \quad (28)$$

$$= \text{constant} \times [\text{Ag}^+]^n \quad (24)$$

$$\therefore \text{pH} = -0.5n \log [\text{Ag}^+] + \text{constant} \quad (29)$$

Two plots of this type prepared using the data summarized in Table VIII are presented in Figure 24, and indicate that the rate of CO-reduction of unbuffered  $\text{AgClO}_4$  solution is second-order in  $[\text{Ag}^+]$ . In constructing Figure 24 no account was taken of the possible effect on  $k_2'''$  of ionic strength which varied from about 0.05 to 1.0 throughout the experimental series (but remained essentially constant during each individual experiment).

Rate measurements of the CO-reduction of unbuffered  $\text{AgClO}_4$  solutions, assuming a first-order dependence on  $P_{\text{CO}}$ , are consistent with a one-term experimental rate law of the form:

$$R_{\text{O}} = -d[\text{CO}]/dt = 0.5 d[\text{H}^+]/dt \quad (30)$$

$$= k_2'' [\text{Ag}^+]^2 P_{\text{CO}} / [\text{H}^+] \quad (31)$$

$$\text{or } R_{\text{O}}' = k_2'' [\text{Ag}^+]^2 / [\text{H}^+] \quad (32)$$

Equation 32 is of the same form as equation 22, thus supporting the experimental rate law developed to represent the rate of CO-reduction of acetate-buffered  $\text{AgClO}_4$  solution. From a comparison of equations 32, 22 and 24 it is evident that:

$$k_2'' = k_2' K_i \quad (33)$$

$$k_2'' = 0.5 k_2''' / [\text{Ag}^+]^2 P_{\text{CO}} \quad (34)$$

Average values of  $k_2''$  calculated using equation 34 are included in Table VIII and lie in the range  $8.3 - 12.3 \times 10^{-9} \text{ atm}^{-1} \text{ sec}^{-1}$ . The 40% variation in  $k_2''$  may be due largely to ionic strength effects particularly with the solution 0.96 M in  $\text{AgClO}_4$ . The average of the other three values is  $8.8 \times 10^{-9} \text{ atm}^{-1} \text{ sec}^{-1}$  and may be compared with a  $k_2'$  of  $3.0 \pm 1.5 \times 10^{-4} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$

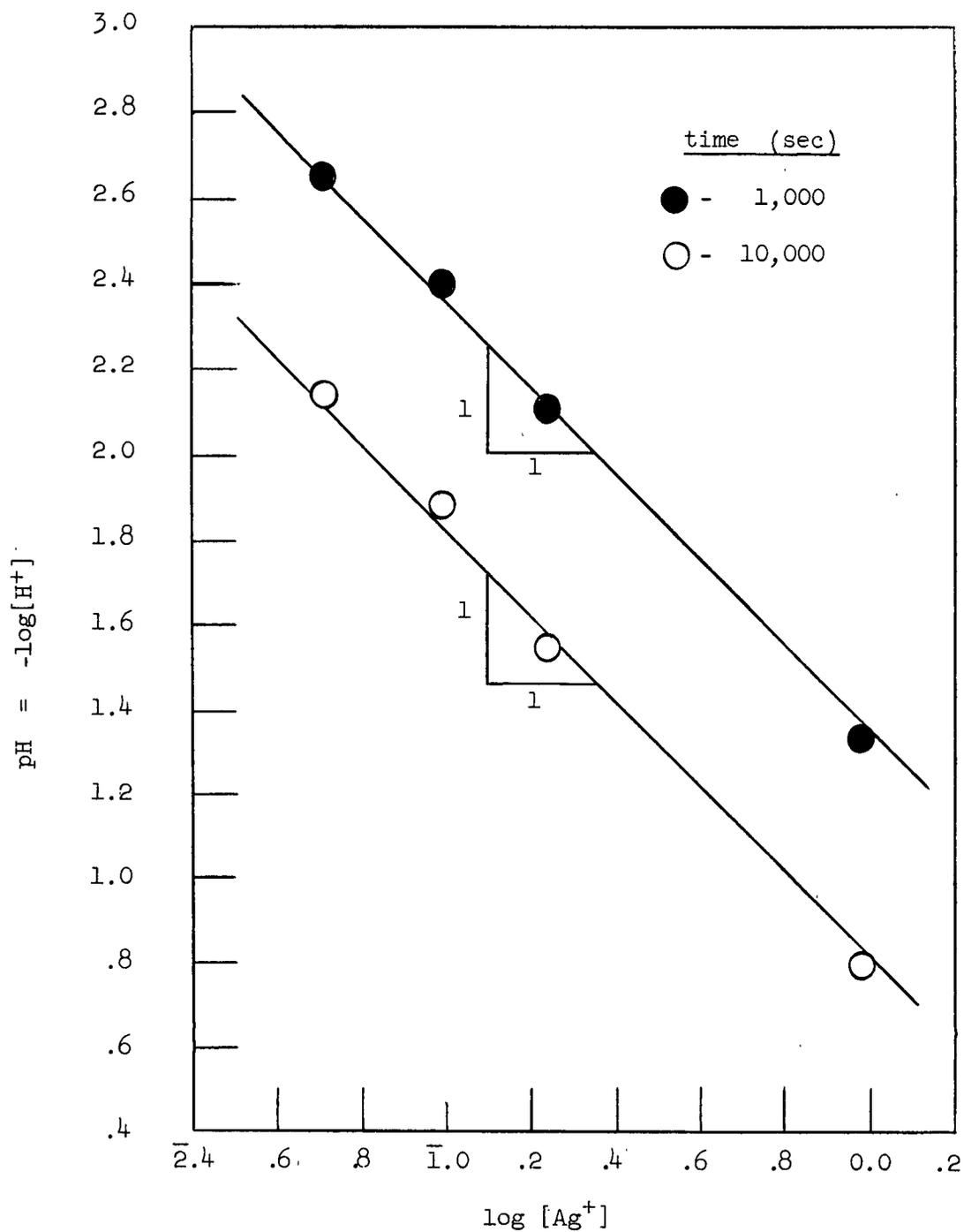


Figure 24. Dependence of Rate on  $[\text{Ag}^+]$  in Unbuffered Solution (53 atm; 90°C)

estimated in Section III-8 for the acetate-independent reaction in buffered solutions. Thus from equation 33  $K_i$  should have a value of about  $3 \times 10^{-5}$  M to make the rate measurements in the buffered and unbuffered systems consistent.

The above result is in agreement with accepted values for  $K_i$  taking into account the effect of ionic strength on the ionization of weak acids in aqueous solution. For example the ionization constant of HOAc in NaCl solution at 25°C varies from  $1.75 \times 10^{-5}$  to a maximum of  $3.32 \times 10^{-5}$  between an ionic strength of zero and 0.5 (41). The effect of temperature causes the value of  $K_i$  for HOAc in water to pass through a maximum of  $1.76 \times 10^{-5}$  at about 25°C and fall to  $1.55 \times 10^{-5}$  at 60°C (41). Extrapolation of this data to 90°C yields a value of about  $1.2 \times 10^{-5}$ . Thus it appears from a comparison of the rates of CO-reduction of  $\text{AgClO}_4$  in buffered and unbuffered solutions that the ionic strength rather than the temperature has a greater effect on the ionization of acetic acid in HOAc-NaOAc solutions at 90°C.

The results of the rate measurements made in buffered and unbuffered solutions are in good agreement considering particularly the widely different methods used to obtain the measurements and the approximately hundred-fold difference in overall rate.

### III-10 "Best Value" Rate Parameters at 90°C

The CO-reduction of  $\text{AgClO}_4$  in acetate-buffered solution is consistent with a rate law represented by equations 19 and 20:

$$R' = k_1' [\overline{\text{AgOAc}}] + k_2' [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3' [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (19)$$

$$R = k_1 [\text{CO}] [\overline{\text{AgOAc}}] + k_2 [\text{CO}] [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3 [\text{CO}] [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (20)$$

Values for the rate constants at 90°C in equation 19, found by graphical analysis in Sections III-6, III-7 and III-8 are summarized in Table IX\*. Also included are the results of least square regression analyses on equation 19 using various sets of experimental data. The regression coefficients were evaluated on an IBM 1620 digital computer using a slightly modified S3-4 statistical analysis program available from the program library of the U.B.C. Computing Centre. Unfortunately the program considers the experimental rate data to have equal possible errors on an absolute rather than a relative basis and thus the higher values of R' are given undue weight.

From consideration of the various sets of rate parameters derived by graphical and statistical methods and summarized in Table IX, a set of "best value" parameters at 90°C for equations 19 and 20 have been selected and presented in Table X. The reliability of the acid-independent parameter is estimated to be  $\pm 25\%$  while the reliability of each of the two acid-dependent parameters is estimated to be  $\pm 50\%$ .

As a further verification of the proposed rate law, equation 19 was integrated numerically using the "best value" rate constants from Table X and compared with the pressure records of several extended reduction experiments. Figure 25 shows the results for five experiments, two of which represent about 50% reduction of  $\text{AgClO}_4$ . Experiments of longer duration were not made because of the possibility of minute gas leaks producing erroneous results for extended measurements of slow rates. A sample calculation for the numerical integration is given in Appendix F. The calculated pressure-time curves are in good agreement with the experimental curves and thus equation 19, developed from measurements of initial rates, is adequate to describe the CO-reduction of  $\text{AgClO}_4$  in acetate-buffered solutions for at least 50% reaction.

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\* The rate constants in equation 20 can be obtained by dividing the corresponding constants in equation 19 by  $\alpha_{\text{CO}} = 6.9 \times 10^{-4} \text{ M/atm}$ .

TABLE IX

Summary of Rate Parameters for Equation 19\* at 90°C

	No of Expts	Rate Parameters			Reference
		$k_1' \times 10^5$ $a^{-1} s^{-1}$	$k_2' \times 10^4$ $M^{-1} a^{-1} s^{-1}$	$k_3' \times 10^4$ $M^{-1} a^{-1} s^{-1}$	
Varied [HOAc] at constant [NaOAc] and [AgClO <sub>4</sub> ] Series A-0	67	2.5 ± 0.6	--	--	Figures 14, 15
	67	--	0.7 ± 0.7	9.0 ± 2.1	Figure 18
	67	3.0	0.9	5.7	Regression Analysis
Varied [NaOAc] at constant [AgClO <sub>4</sub> ] and [HOAc]/[NaOAc] Series P-Y	31	--	3.0 ± 1.5	--	Figure 22
	31	2.3	2.5	3.0	Regression Analysis
All Experiments	119	3.0	1.4	5.8	Regression Analysis

Equation 19

$$R' = k_1' [\overline{AgOAc}] + k_2' [Ag^+]^2 \frac{[OAc^-]}{[HOAc]} + k_3' [Ag^+] [\overline{AgOAc}] \frac{[OAc^-]}{[HOAc]}$$

\* To obtain rate parameters in terms of [CO] divide values in Table IX

by  $\alpha_{CO} = 6.9 \times 10^{-4} M/atm.$

TABLE X

"Best Value" Rate Parameters at 90°C

Equation 19	Equation 20	Reliability
$k_1' = 2.7 \times 10^{-5} \text{ a}^{-1} \text{ s}^{-1}$	$k_1 = 0.04 \text{ M}^{-1} \text{ s}^{-1}$	$\pm 25\%$
$k_2' = 2.1 \times 10^{-4} \text{ M}^{-1} \text{ a}^{-1} \text{ s}^{-1}$	$k_2 = 0.3 \text{ M}^{-2} \text{ s}^{-1}$	$\pm 50\%$
$k_3' = 6.2 \times 10^{-4} \text{ M}^{-1} \text{ a}^{-1} \text{ s}^{-1}$	$k_3 = 0.9 \text{ M}^{-2} \text{ s}^{-1}$	$\pm 50\%$

Equation 19

$$R' = k_1' [\overline{\text{AgOAc}}] + k_2' [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3' [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

Equation 20

$$R = k_1 [\text{CO}] [\overline{\text{AgOAc}}] + k_2 [\text{CO}] [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3 [\text{CO}] [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

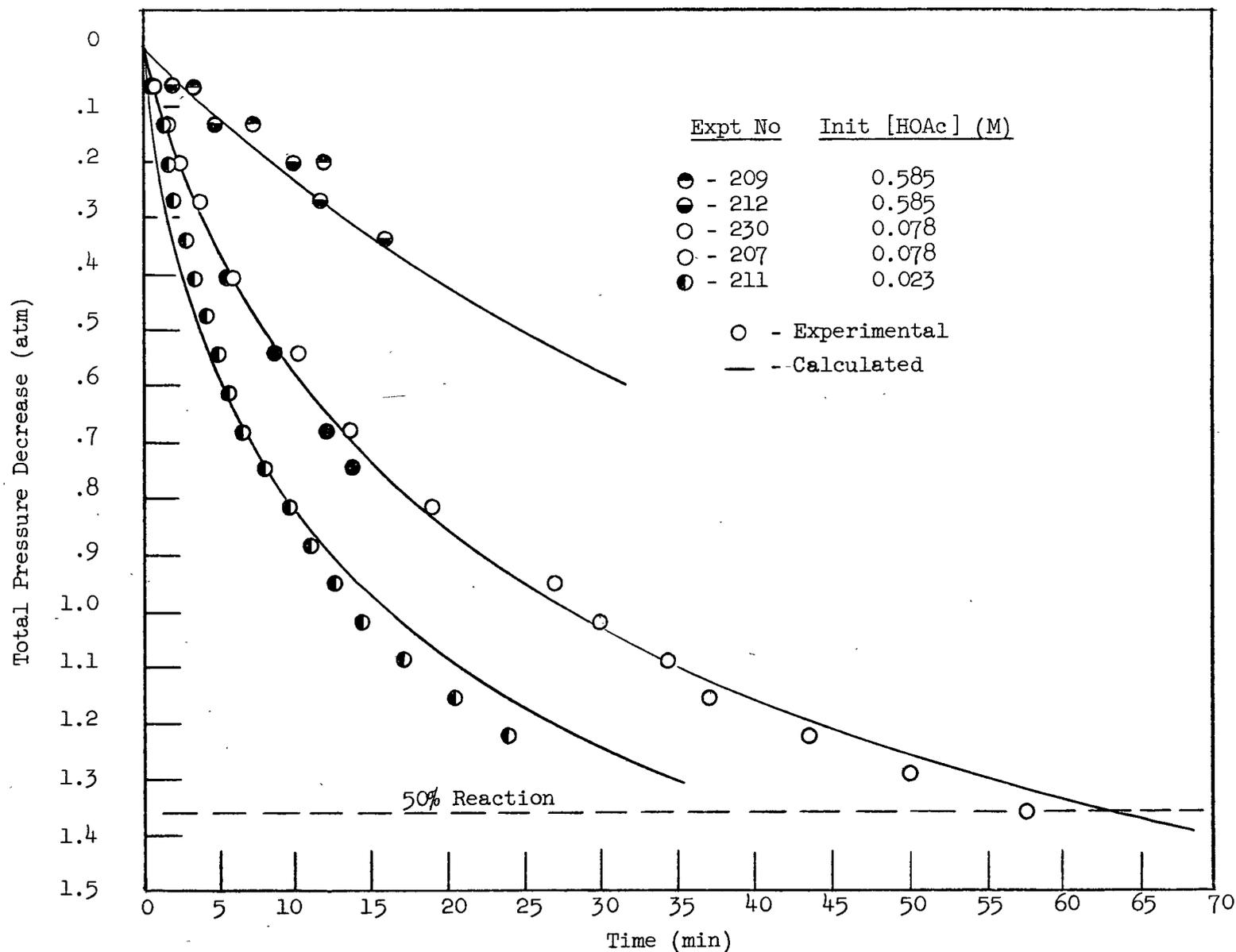


Figure 25. Comparison of Experimental and Calculated Pressure Records (Initial Conditions: 0.115 M  $\text{AgClO}_4$ ; 0.195 M  $\text{NaOAc}$ ; 5.4 atm  $\text{CO}$ ;  $90^\circ\text{C}$ )

III-11 Proposed Mechanism

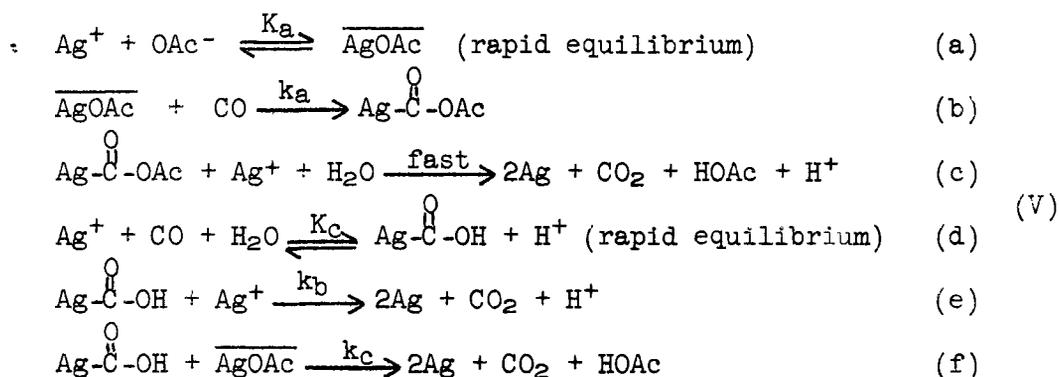
The kinetics of the CO-reduction of acetate-buffered AgClO<sub>4</sub> solutions are described by the experimental rate law:

$$R = k_1[\text{CO}][\overline{\text{AgOAc}}] + k_2[\text{CO}][\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3[\text{CO}][\text{Ag}^+][\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (20)$$

In terms of [H<sup>+</sup>] equation 20 may be re-written as:

$$R = k_1[\text{CO}][\overline{\text{AgOAc}}] + k_2K_1 \frac{[\text{CO}][\text{Ag}^+]^2}{[\text{H}^+]} + k_3K_1 \frac{[\text{CO}][\text{Ag}^+][\overline{\text{AgOAc}}]}{[\text{H}^+]} \quad (35)$$

A mechanism which is consistent with equation 35 can be represented by the following scheme:



The rate law derived from this sequence corresponds to:

$$R = \frac{-d[\text{CO}]}{dt} = k_a[\text{CO}][\overline{\text{AgOAc}}] + k_bK_c \frac{[\text{CO}][\text{Ag}^+]^2}{[\text{H}^+]} + k_cK_c \frac{[\text{CO}][\text{Ag}^+][\overline{\text{AgOAc}}]}{[\text{H}^+]} \quad (36)$$

which is identical with equation 35 if  $k_a = k_1$ ,  $k_bK_c = k_2K_1$ ,  $k_cK_c = k_3K_1$  and if [H<sub>2</sub>O] is incorporated in K<sub>c</sub>.

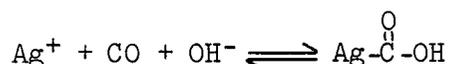
Support for the nature of the proposed intermediates is drawn from studies on the CO-reduction of Hg<sup>++</sup> in dilute HClO<sub>4</sub> (15), the reduction of Ag(I) amines in basic solution (14), and the Hg<sup>++</sup> and Ag<sup>+</sup> catalyzed reductions of MnO<sub>4</sub><sup>-</sup> in both acid and basic solution (15). Analogous intermediates were proposed in these cases with the evidence for (Hg- $\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ )<sup>+</sup> being particularly

strong because of the existence of the stable methyl formate derivative  $\text{AcO-Hg-C(=O)-OCH}_3$  formed when CO reacts with methanolic solutions of  $\text{Hg(OAc)}_2$  (30). The oxidation of CO in aqueous solution is apparently facilitated by the presence of an oxygen-donating base (e.g.  $\text{OH}^-$ ,  $\text{OAc}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{MnO}_4^-$ ).

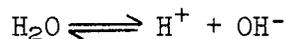
The reduction of silver acetate by a pH-independent mechanism is similar to the reduction of  $\text{Hg}^{++}$  and  $\text{MnO}_4^-$  (see mechanism III, Section I-4), while the pH-dependent contribution is similar to the reduction of silver amines in basic solution (see mechanism II, Section I-4). In the latter case the formation of the  $\text{LAg-C(=O)-OH}$  complex (where L denotes an amine ligand) is rate-determining as evidenced by a first-order dependence on  $[\text{Ag(I)}]$  and  $[\text{OH}^-]$ . Apparently at  $[\text{NH}_4^+]$  greater than 0.02 M (i.e. lower pH) with  $\text{NH}_3$  as the amine ligand the decomposition of the complex to form final products is retarded to the extent that the rate is determined by competition between this step and a back-reaction to form initial reactants. In the reduction of Ag(I) in acid solution the rate of complex decomposition to products relative to back-reaction to form initial reactants must be decreased even further until the complex formation becomes a pre-equilibrium and the rate is determined exclusively by attack of another Ag(I) species (e.g.  $\text{Ag}^+$  or  $\text{AgOAc}$ ) on the complex to form final products.

A hydrolyzed silver(I) species (e.g.  $\text{AgOH}$ ) is not required to explain the observed kinetics in acid solution. The association constant  $K_h$  of  $\text{Ag}^+$  and  $\text{OH}^-$  is given as about  $10^4$  at room temperature in dilute solution (42). Thus while  $\text{LAgOH}$  is the predominant silver species in basic amine solutions (assuming  $K_h$  for  $\text{AgL}^+$  is of the same order as for  $\text{Ag}^+$ )  $\text{AgOH}$  is present only in trace amounts in acid solution.

In the proposed mechanism for reduction of Ag(I) in acid solution reaction V(d) is indistinguishable from

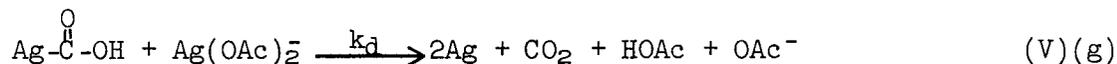


preceded by the water dissociation equilibrium:

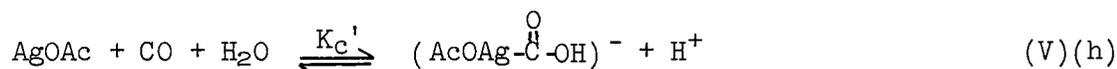


The pH effect arises in an equilibrium preceding the rate-controlling step and therefore its exact nature cannot be determined from the present kinetic study.

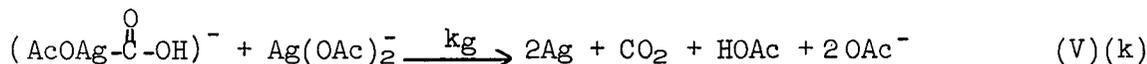
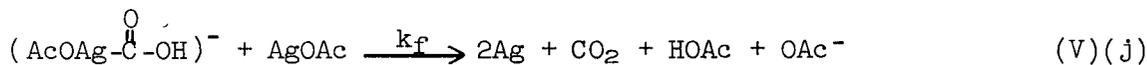
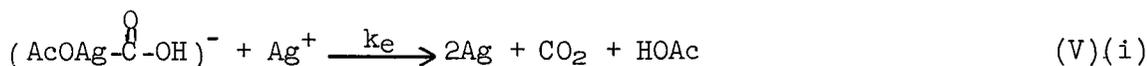
The mechanism proposed to describe the CO-reduction of  $\text{AgClO}_4$  is probably the simplest which is consistent with the present kinetic study in both unbuffered and acetate-buffered solutions. Further contributions of silver-acetate complexes can be proposed but it is difficult to assess their validity on an experimental basis. For example  $\text{Ag}(\text{OAc})_2^-$  might attack the intermediate complex formed in V(d) by a reaction parallel to V(e) and V(f), viz:



Also  $\text{AgOAc}$  might form an intermediate by an equilibrium analogous to V(d), viz:



This intermediate could be attacked through processes parallel to reactions V(e), V(f) and V(g), viz:



If the association constants of  $\text{AgOAc}$  and  $\text{Ag}(\text{OAc})_2^-$  from  $\text{Ag}^+$  and  $\text{OAc}^-$  are represented by  $K_1$  and  $K_2$  respectively and  $[\text{H}_2\text{O}]$  is incorporated in each of  $K_c$  and  $K_c'$ , the acid-dependent reduction rate, considering all contributions from

reaction V(d) to V(k), can be represented by:

$$D = \frac{[\text{CO}][\text{Ag}^+]^2}{[\text{H}^+]} \left( k_b K_c + (k_c K_c K_1 + k_e K_c' K_1) [\text{OAc}^-] + (k_d K_c K_2 + k_f K_c' K_1 K_1) [\text{OAc}^-]^2 + k_g K_c' K_1 K_2 [\text{OAc}^-]^3 \right) \quad (37)$$

The sum of the constants of like terms in equation 37 can be defined by new parameters  $C_n$  ( $n = 1, 2, 3, 4$ ) and the expression reduced to equation 38 which represents a power series in  $[\text{OAc}^-]$  to describe the kinetics of the pH-dependent CO-reduction of acetate-buffered  $\text{AgClO}_4$  solutions.

$$D = \frac{[\text{CO}][\text{Ag}^+]^2}{[\text{H}^+]} \sum_{n=1}^4 C_n [\text{OAc}^-]^{n-1} \quad (38)$$

By a suitable choice of parameters equation 38 can be fitted to almost any set of rate measurements, be they good or bad, with a high degree of precision. Graphical analyses of the measurements made in the present investigation are consistent with a rate expression to describe the pH-dependent reaction that involves only the initial two terms in equation 38 and reactions V(d), V(e) and V(f) give rise to a rate law of this form.

Similar considerations to those presented above can be applied to the acid-independent reduction process and again it is concluded that the rate law arising from reaction V(b) is of the simplest form consistent with experimental observation.

Many ions with a  $d^{10}$  structure, including  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Au}^+$  and  $\text{Hg}^{++}$ , tend to form linearly co-ordinated complexes\* and thus it is unlikely that  $\text{Ag}(\text{OAc})_2^-$  is capable of reacting without prior dissociation to form an intermediate complex similar to those described by reactions V(d) and V(h). For

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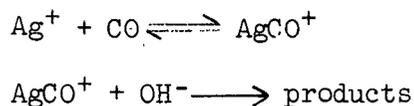
\* It has been suggested (43) that this effect is due to hybridization of d and s orbitals which remove charge from the region between the metal ion and its ligands and thus favours linear co-ordination for those  $d^{10}$  ions with sufficiently low d-s separations.

similar reasons it is doubtful that the  $\text{Ag}(\text{OAc})_3^-$  complex proposed to help explain some equilibria studies in aqueous solutions (44) plays a role in the reduction mechanism, if in fact the complex exists. In the interpretation of another study on equilibria in aqueous silver acetate solutions an  $\text{Ag}_2\text{OAc}^+$  complex has been postulated (45). The existence of such a complex reflects an affinity of  $\text{AgOAc}$  for another silver ion. Because of the higher basicity of water compared to  $\text{HOAc}$ , which is analogous to  $\text{AgOAc}$ , this second silver ion should strongly prefer to remain in the simple hydrated form, and therefore the existence of significant concentrations of  $\text{Ag}_2\text{OAc}^+$  is doubted.

The amount of silver present in the various acetate complexes has been approximated by an average  $[\overline{\text{AgOAc}}]$  calculated from a mean association constant ( $K_a$ ). If the reactivity of  $\text{AgOAc}$  and  $\text{Ag}(\text{OAc})_2^-$  were significantly different deviations from the proposed rate law would be expected particularly at high  $[\text{OAc}^-]$ . Reference to Figure 18, Section III-7, in which  $S'/[\text{Ag}^+]^2[\text{OAc}^-]$  is plotted against  $[\text{OAc}^-]$ , shows that no deviation in the acid-dependent rate expression is apparent at  $[\text{OAc}^-]$  up to about 0.8 M, where  $\text{AgOAc}$  and  $\text{Ag}(\text{OAc})_2^-$  should be present in approximately equal concentrations, based on published room temperature complexity constants (38). It is therefore concluded that  $\text{AgOAc}$  and  $\text{Ag}(\text{OAc})_2^-$  are approximately equally reactive in the pH-dependent reduction process. Reference to Figure 14, Section III-6, in which  $I'/[\text{Ag}^+]$  is plotted against  $[\text{OAc}^-]$ , gives some evidence that  $\text{Ag}(\text{OAc})_2^-$  may be more reactive than  $\text{AgOAc}$  toward direct attack by  $\text{CO}$ .

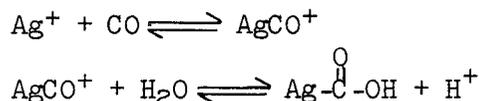
Silver carbonyl intermediates have been proposed to explain the experimentally observed rate of  $\text{CO}$ -reduction of dilute  $\text{Ag}_2\text{SO}_4$  solutions buffered with 0.65 M  $\text{NH}_4\text{OAc}$  (13). At the concentrations used the majority of the silver was complexed with ammonia. The effect of pH was not investigated and thus a first-order dependence on  $[\text{CO}]$  and an apparent second-order dependence on  $[\text{Ag(I)}]$  was taken as evidence for the rate-determining step involving

the reaction of H<sub>2</sub>O with Ag<sub>2</sub>CO<sup>++</sup> formed in a pre-equilibrium (see mechanism I, Section I-4). More recent studies (14) have shown that at [NH<sub>4</sub><sup>+</sup>] greater than about 0.02 M the reduction of Ag(NH<sub>3</sub>)OH<sup>+</sup> approaches second-order in both [Ag(I)] and [OH<sup>-</sup>]. In this latter case a mechanism involving NH<sub>3</sub>Ag-C(=O)-OH as an intermediate was proposed. The existence of a silver carbonyl complex is still feasible particularly since analogous stable Cu(I) carbonyl complexes are known (25). Thus the observed kinetics for the CO-reduction of unbuffered AgClO<sub>4</sub> might be explained by a mechanism similar to:



A rate law developed from this scheme using the steady-state approximation for [AgCO<sup>+</sup>] successfully described the experimental observations in unbuffered solution. When acetate contributions were considered, however, a satisfactory simple expression could not be developed. It was therefore concluded that such a mechanism is not responsible for the CO-reduction of Ag(I) in acid solution.

Silver carbonyl complexes formed in pre-equilibria might take part in the formation of Ag-C(=O)-OH in V(d), e.g.:



This implies that a CO molecule first co-ordinates with an Ag<sup>+</sup> ion before reacting further with an H<sub>2</sub>O molecule to form the Ag-C(=O)-OH intermediate. Kinetically, such a process is indistinguishable from the direct insertion of CO between Ag<sup>+</sup> and a co-ordinated H<sub>2</sub>O molecule.

Silver hydride complexes, which are postulated to be active intermediates in H<sub>2</sub>-reduction processes in aqueous solution (46,47), apparently do

not influence the kinetics of corresponding CO-reduction processes. The mechanism by which each gas reacts with Ag(I) is specific; H<sub>2</sub> is activated by dissociation, while CO is oxidized by the transfer of an oxygen atom from a donor-base (e.g. H<sub>2</sub>O, OAc<sup>-</sup>). In both cases basic ligands increase the metal ion reactivity through stabilization of protons released in the reduction processes.

It is unlikely that nucleation or growth of silver crystals influence the reduction kinetics. Nucleation generally involves a high-order dependence on metal ion concentration, for example, the disproportionation of Cu(I) is tenth-order in [Cu(I)] (48), and growth rates for most metals are also fast as evidenced by low overvoltages required for electrodeposition (49). Trace amounts of precipitated silver from previous experiments were usually present in the reactor and served to minimize possible nucleation effects.

### III-12 Effect of Temperature

The effect of temperature on the rate of CO-reduction of AgClO<sub>4</sub> in acetate-buffered solution was determined at 60, 80, 90 and 110°C by measuring the rate of CO consumption at a constant degree of acetate complexing at a number of HOAc concentrations. The results of these measurements are shown as R' vs [HOAc]<sup>-1</sup> plots in Figure 26 and summarized in Table XI. In Section III-4 the overall reaction was shown to be made up of an acid-independent and an acid-dependent component, i.e.:

$$R' = I' + D' \quad (6)$$

$$= I' + S'/[\text{HOAc}] \quad (5)$$

Analysis of the intercepts of R' vs [HOAc]<sup>-1</sup> plots at 90°C indicated that:

$$I' = k_1'[\overline{\text{AgOAc}}] \quad (7)$$

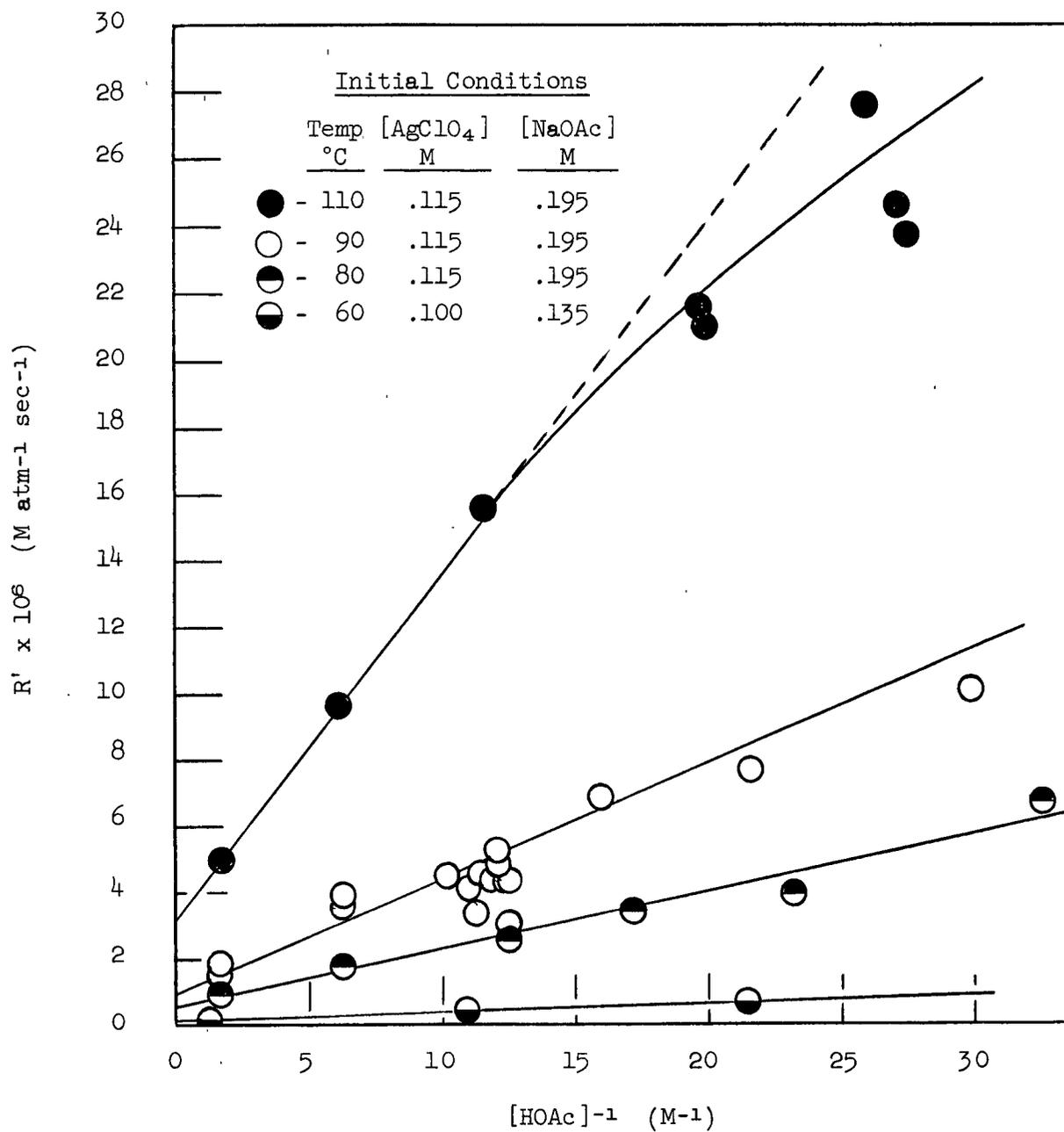


Figure 26. Dependence of Rate on  $[\text{HOAc}]^{-1}$  at 60, 80, 90 and 110°C

TABLE XI

Dependence of Reduction Rate on Temperature

Temp °C	$10^3/T$ °K <sup>-1</sup>	[Ag(I)] M	[NaOAc] M	[AgOAc] M	$I' \times 10^6$ M a <sup>-1</sup> s <sup>-1</sup>	$S' \times 10^6$ M <sup>2</sup> a <sup>-1</sup> s <sup>-1</sup>	$k_1' \times 10^6$ a <sup>-1</sup> s <sup>-1</sup>	log $k_1'$	log $S'$
60	3.00	.099	.134	.028	0.14	0.029	5.0	6.70	--
80	2.83	.110	.190	.039	0.64	0.164	16.3	5.21	7.22
90	2.76	.110	.190	.039	0.90	0.320	23.1	5.36	7.51
110	2.61	.105	.185	.037	3.2	1.04	86.5	5.94	6.02

Initial Conditions:

60°C - 0.100 M AgClO<sub>4</sub>; 0.135 M NaOAc; 5 atm CO

80, 90, 110°C - 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc; 5 atm CO

while analysis of the slopes indicated that:

$$S' = k_2' [Ag^+]^2 [OAc^-] + k_3' [Ag^+] [\overline{AgOAc}] [OAc^-] \quad (15)$$

The effect of acetate complexing on the reduction rate was studied only at 90°C and thus it was not possible to calculate the temperature dependence of  $k_2'$  and  $k_3'$  individually. An average activation energy for the acid-dependent reaction was estimated, however, from the slope of a  $\log S'$  vs  $1/T$  plot at a constant degree of complexing. Such a plot is given in Figure 27 for 80, 90 and 110°C and yields an average activation energy of  $17 \pm 3$  kcal/mole. Also included in Figure 27 is a plot of  $\log I' / [\overline{AgOAc}]$  vs  $1/T$  at 60, 80, 90 and 110°C which gives the temperature dependence of  $k_1'$  and yields an activation energy of  $15 \pm 2$  kcal/mole for the acid-independent reaction.

The experimental activation energies incorporate the enthalpies of all equilibria preceding the rate-determining step. In the acid-independent reaction these include the heat of dissolution of CO and the heat of formation of  $\overline{AgOAc}$ , while in the acid-dependent reaction the heat of formation of HOAc and the intermediate complex,  $Ag-\overset{O}{\parallel}C-OH$ , must also be considered. The heats of CO dissolution and  $\overline{AgOAc}$  formation are small (see Appendices B and C) as is the heat of formation of HOAc (e.g.  $-0.1$  kcal/mole at 25°C (44)). No information is available for the heat of formation of the intermediate complex. If  $OH^-$  rather than  $H_2O$  is involved in the formation, the experimental activation energy for the acid-dependent reaction includes the heat of dissociation of  $H_2O$  which is about 14 kcal/mole in dilute aqueous solution (41).

Combining the experimental activation energies with the "best value" rate parameters at 90°C listed in Table X (Section III-10), assuming equal activation energies for each of the acid-dependent reactions, gives the following Arrhenius expressions for the temperature dependence of the rate

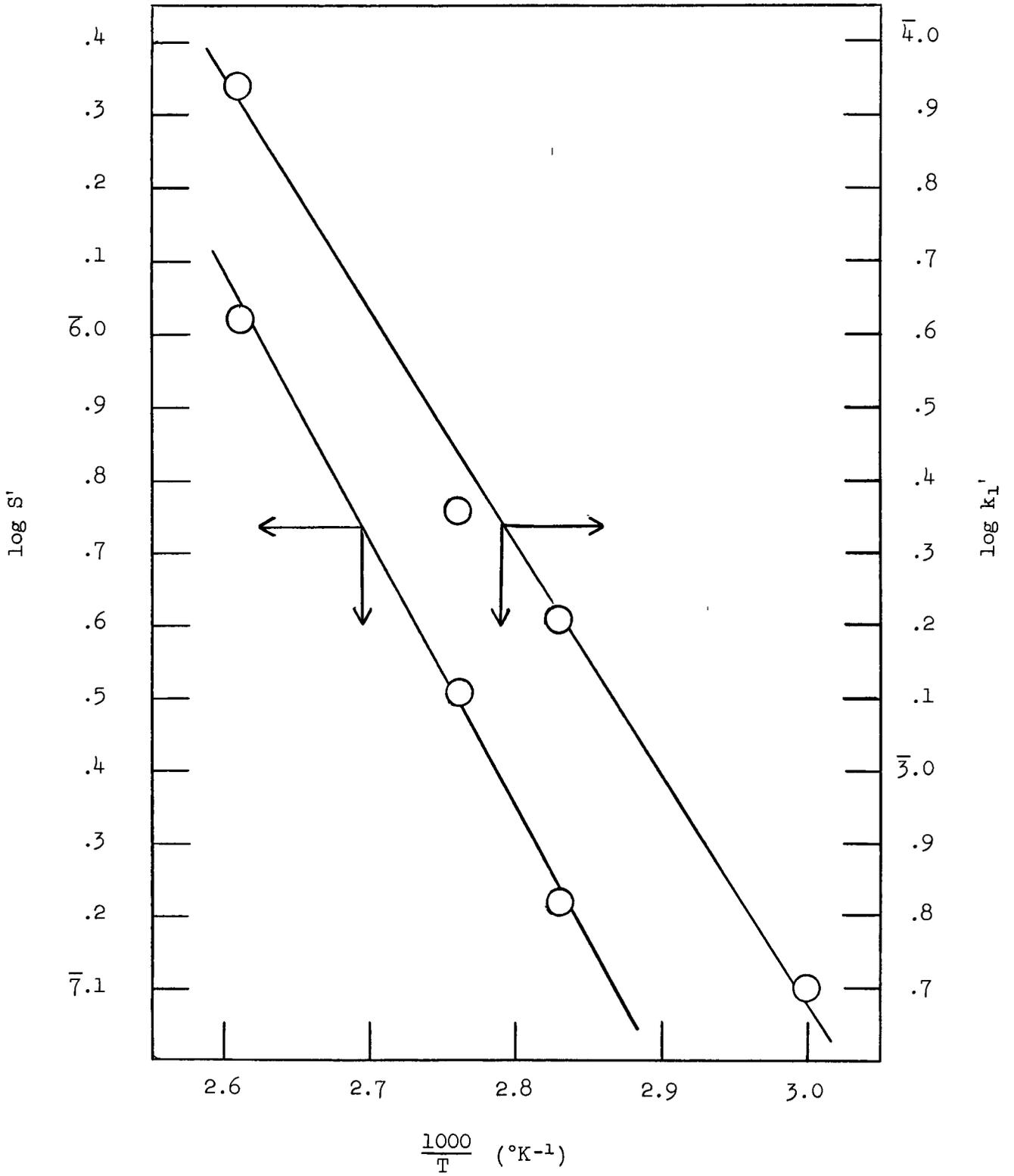


Figure 27. Arrhenius Plots for Acid-Independent and Acid-Dependent Reactions

parameters over the range investigated:

$$k_1 = 107.6 \pm 1.3 \exp[-(15 \pm 2) 10^3/RT] \text{ M}^{-1} \text{ sec}^{-1} \quad (39)$$

$$k_2 = 10^{9.7} \pm 2.0 \exp[-(17 \pm 3) 10^3/RT] \text{ M}^{-2} \text{ sec}^{-1} \quad (40)$$

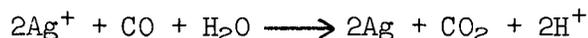
$$k_3 = 10^{10.2} \pm 2.0 \exp[-(17 \pm 3) 10^3/RT] \text{ M}^{-2} \text{ sec}^{-1} \quad (41)$$

The experimental activation entropies corresponding to the frequency factors in the above expressions are:  $\Delta S_1^\ddagger = -26 \pm 6$  e.u.,  $\Delta S_2^\ddagger = -16 \pm 9$  e.u. and  $\Delta S_3^\ddagger = -14 \pm 9$  e.u. (based on a standard state of one mole per litre).

These experimental activation entropies also incorporate contributions from equilibria preceding the rate-determining step. In the acid-independent reaction these contributions may be small and the true activation entropy may correspond to that found from equation 39. This value is abnormally low for a bimolecular reaction (50) and may reflect steric hindrance for the insertion of a CO molecule into the silver-oxygen bond. Alternatively the reactive silver species may not be undissociated AgOAc molecules but rather one present in very low concentration (e.g. ion pairs). A further explanation may involve a large solvent ordering effect in the formation of the activated complex. Such an effect is not generally expected for reaction between undissociated molecules.

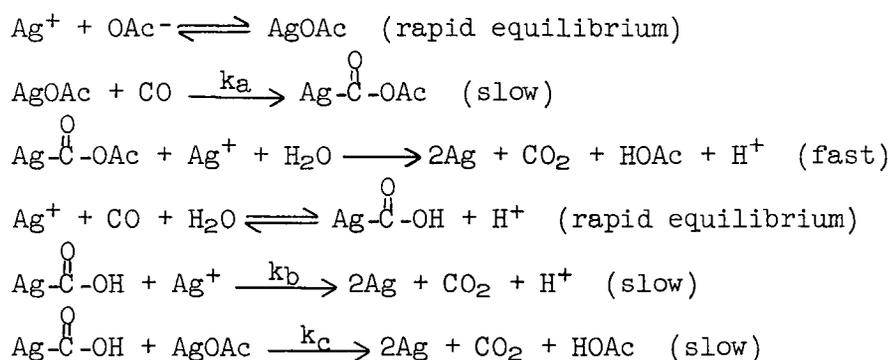
IV CONCLUSION

The CO-reduction of silver perchlorate in acid solution is described by the overall reaction:



In acetate-buffered solution the reaction proceeds homogeneously in the liquid phase by two parallel routes, one of which is pH-independent and the other, pH-dependent. The pH-dependent route is favoured by increased pH and is made up of both an acetate-independent and acetate-dependent contribution.

The observed kinetics are consistent with the following mechanism:



In the pH-dependent reaction the reactivity of silver-acetate complexes is about a factor of three greater than the reactivity of simple hydrated silver ions. This enhanced reactivity is attributed to stabilization by the basic acetate anion of the proton released in the reduction process.

Buffering silver perchlorate solutions with sodium acetate and acetic acid increases the reduction rate by (i) increasing the pH, (ii) increasing the reactivity of silver ions in the pH-dependent reaction through complexing and (iii) providing an alternate pH-independent route for reduction. The effect of increased pH is much greater than the specific effects of

silver-acetate complexing.

The CO-reduction of silver(I) in acid solution is consistent with the formation of intermediate complexes by the insertion of a CO molecule between a silver ion and co-ordinated oxygen-donating base.

APPENDIX A

METHOD OF ESTIMATING RATES FROM THE SLOPE OF PRESSURE-TIME RECORDS

The slope of a total pressure vs time record (e.g. Figure 4, Section III-1) can be converted to the rate of CO consumption in fundamental units (e.g. M sec<sup>-1</sup>) from a knowledge of (i) the gas-liquid ratio in the reactor, (ii) the solubility of CO and CO<sub>2</sub> under the experimental conditions and (iii) the stoichiometric relationship between the consumption of CO and the production of CO<sub>2</sub>. The mathematical expression used for this conversion is given by equation A-1:

$$\frac{-d[\text{CO}]}{dt} = \frac{-dP_T}{dt} \left( \frac{(F + \alpha_{\text{CO}})(F + \alpha_{\text{CO}_2})}{(\alpha_{\text{CO}_2} - \alpha_{\text{CO}})} \right) \quad (\text{A-1})$$

where

$-d[\text{CO}]/dt$  = rate of CO consumption (M sec<sup>-1</sup>)\*

$dP_T/dt$  = slope of a pressure-time record (atm sec<sup>-1</sup>)

$\alpha_{\text{CO}}$  = solubility of CO (M/atm)\*

$\alpha_{\text{CO}_2}$  = solubility of CO<sub>2</sub> (M/atm)\*

and  $F$  = a gas-liquid volume factor (M atm)

$$= (V_g/V_l)(1000/RT)$$

where  $V_g$  = gas volume (mls) measured at experimental temperature

$V_l$  = liquid volume (mls) measured at room temperature

$R$  = universal gas constant (82.05 mls atm mole<sup>-1</sup> deg<sup>-1</sup>)

$T$  = experimental temperature (°K)

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\* Concentrations are expressed in terms of litres of solution measured at room temperature (20-25°C).

The derivation of equation A-1 is given below.

A particular gas (e.g. CO or CO<sub>2</sub>) present in the reactor will be distributed between the gas and liquid phase in fixed proportion dependent on the ratio of gas and liquid volumes and on the solubility of the gas in the liquid phase. Assuming that the ideal gas law applies with sufficient accuracy at the temperature and pressure of interest, the concentration of a gas in the gas phase is given by:

$$\begin{aligned} [\text{gas}]_g &= \frac{PV_g}{RT} \text{ (moles per } V_1 \text{ mls of solution)} \\ &= P \times \frac{V_g \cdot 1000}{V_1 RT} \text{ (moles per litre of solution)} \\ &= F \times P \end{aligned}$$

where P = partial pressure of gas (atm).

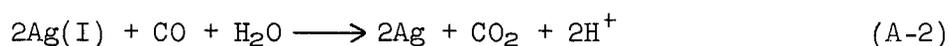
The concentration of a gas in the liquid phase is given by Henry's law:

$$[\text{gas}]_l = \alpha \times P \text{ (moles per litre of solution)}$$

Thus the total concentration of a particular gas present in the reactor is

$$[\text{gas}] = P(F + \alpha)$$

From the stoichiometry of the Ag(I)-CO reaction in acid solution, viz:



the quantity of CO consumed equals the quantity of CO<sub>2</sub> produced. Thus the change in concentration of each gas is given by:

$$\begin{aligned} X &= \Delta[\text{gas}] \\ &= \Delta P_{\text{CO}} (F + \alpha \text{CO}) \\ &= \Delta P_{\text{CO}_2} (F + \alpha \text{CO}_2) \end{aligned}$$

The observed pressure change during a reduction experiment is the difference between the decrease in CO pressure and the increase in CO<sub>2</sub> pressure, i.e.:

$$\begin{aligned} \Delta P_T &= \Delta P_{CO} - \Delta P_{CO_2} \\ &= \frac{X}{(F + \alpha_{CO})} - \frac{X}{(F + \alpha_{CO_2})} \\ &= X \left( \frac{(\alpha_{CO_2} - \alpha_{CO})}{(F + \alpha_{CO})(F + \alpha_{CO_2})} \right) \\ \text{or } \Delta[CO] &= \Delta P_T \left( \frac{(F + \alpha_{CO})(F + \alpha_{CO_2})}{(\alpha_{CO_2} - \alpha_{CO})} \right) \end{aligned}$$

Thus the rate of CO consumption is given by:

$$\frac{-d[CO]}{dt} = \frac{-dP_T}{dt} \left( \frac{(F + \alpha_{CO})(F + \alpha_{CO_2})}{(\alpha_{CO_2} - \alpha_{CO})} \right) \quad (A-1)$$

The values for the solubility coefficients used in equation A-1 were obtained from measurements described in Appendix B and are summarized in Table A-I.

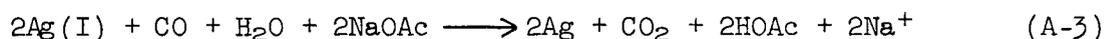
TABLE A-I

Solubility of CO and CO<sub>2</sub> in Water at 60, 80, 90 and 110°C

Temp °C	$\alpha_{CO} \times 10^4$ M/atm	$\alpha_{CO_2} \times 10^4$ M/atm
60	7.0	163.5
80	6.8	122.5
90	6.9	105.0
110	7.3	84.0

The gas volume in each experiment was estimated by subtraction from the total volume of the reactor system, the initially added volume of solution, corrected to the experimental temperature using the variation in density of water with temperature (51). The volume of the reactor system was determined at each experimental temperature from the sum of the gas volume measured from several observed decreases in pressure due to CO saturation when the reactor was about 90% filled with water, plus the volume of water present in the reactor during each determination. Reactor volumes determined in this way were estimated to be accurate to  $\pm 0.3$  mls in a total volume of about 120 mls (e.g. 118.9 at 60°, 119.5 at 80°, 120.0 at 90°, 120.1 at 110° and 120.7 at 120°C).

Corrections to the initial concentrations of  $\text{AgClO}_4$ ,  $\text{NaOAc}$ ,  $\text{HOAc}$  and  $\text{CO}$  to take account of the small amount of reaction which occurred during  $\text{CO}$  saturation were made on the basis of the stoichiometry of reaction A-3 using the initial rates calculated from equation A-1.



#### Sample Calculation

Expt No 285 (Figure 4, Section III-1, Curve C; see also Appendix D-III-I)

Initial Conditions: 0.235 M  $\text{AgClO}_4$ ; 0.090 M  $\text{NaOAc}$ ; 0.090 M  $\text{HOAc}$ ;

12.8 atm  $\text{CO}$ ; 90°C

Initial Slope ( $dP_T/dt$ ) =  $-5.76 \times 10^{-3}$  atm  $\text{sec}^{-1}$  after 2-1/4 min

Gas Solubility at 90°C  $\alpha_{\text{CO}} = 6.9 \times 10^{-4}$  M/atm

$\alpha_{\text{CO}_2} = 105.0 \times 10^{-4}$  M/atm

Volume of solution added ( $V_1$ ) = 101.5 mls

Total volume of reactor at 90°C = 120.0 mls

Density of  $\text{H}_2\text{O}$  = 0.9653 g/ml at 90°C; 0.9982 g/ml at 20°C

$$\therefore V_g = 120.0 - 101.5 \times 0.9982/0.9653 = 15.1 \text{ mls}$$

$$\therefore F = \frac{15.1}{101.5} \times \frac{1000}{82.05 \times 363} = 49.9 \times 10^{-4} \text{ M/atm}$$

$$\begin{aligned} \therefore \frac{-d[\text{CO}]}{dt} &= 5.76 \times 10^{-3} \left( \frac{(49.9 + 6.9) 10^{-4} (49.9 + 105.0) 10^{-4}}{(105.0 - 6.9) 10^{-4}} \right) \\ &= 51.8 \times 10^{-6} \text{ M sec}^{-1} \end{aligned}$$

Using this rate value an estimate can be made of the amount of  $\text{AgClO}_4$ ,  $\text{NaOAc}$  and  $\text{CO}$  consumed and the  $\text{HOAc}$  produced at the point the slope was measured.

$$\begin{aligned} -0.5 \Delta[\text{AgClO}_4] &= -0.5 \Delta[\text{NaOAc}] = -\Delta[\text{CO}] = 0.5 \Delta[\text{HOAc}] \\ &= 2^{-1/4} \times 60 \times 51.8 \times 10^{-6} = 0.007 \text{ M} \end{aligned}$$

The concentrations at the point the rate was measured are therefore estimated to be

$$[\text{Ag(I)}] = 0.235 - 0.014 = 0.221 \text{ M}$$

$$[\text{NaOAc}] = 0.090 - 0.014 = 0.076 \text{ M}$$

$$[\text{HOAc}] = 0.090 + 0.014 = 0.104 \text{ M}$$

$$P_{\text{CO}} = 12.8 - 0.007/(49.9 + 6.9) 10^{-4} = 11.6 \text{ atm}$$

APPENDIX B

SOLUBILITY OF CARBON MONOXIDE, CARBON DIOXIDE AND HYDROGEN IN WATER

Data for the solubility of carbon monoxide in water are available (52) at atmospheric pressure and temperatures to 100°C while carbon dioxide solubility data are available (53) to 700 atm and 120°C. As an initial phase of the present investigation data on the solubility of carbon monoxide in water were extended to 63 atm and 220°C using the previously described reactor system (Section II-1). The solubility of hydrogen in water was also measured at about 25 atm and temperatures to 225°C. A value for the solubility of CO<sub>2</sub> in water and the salt effect of sodium acetate - acetic acid mixtures were determined at 90°C and 2.6 atm.

Experimental

The gas outlet line inside the reactor was bent so that liquid samples could be drawn through the 1/16-in o.d. capillary tubing and collected over mercury in the 50-ml water-jacketed burette shown in Figure B-1. Sufficient water was charged to the reactor to leave an initial gas volume of about 10 mls at experimental temperature. The head space and water were degassed under vacuum or by boiling the solution and steam flushing at atmospheric pressure. After degassing the outlet valves were closed, the shaking mechanism activated and the solution heated to the desired temperature before introducing carbon monoxide or hydrogen. When equilibrium had been attained (approximately 5 min), the sampling line was flushed with a few mls of solution and a 10 to 30-ml liquid sample collected in the burette while the shaking mechanism was stopped. The burette valves were closed and the excess gas flushed from solution by rapidly raising and lowering the mercury level. After equilibrium had

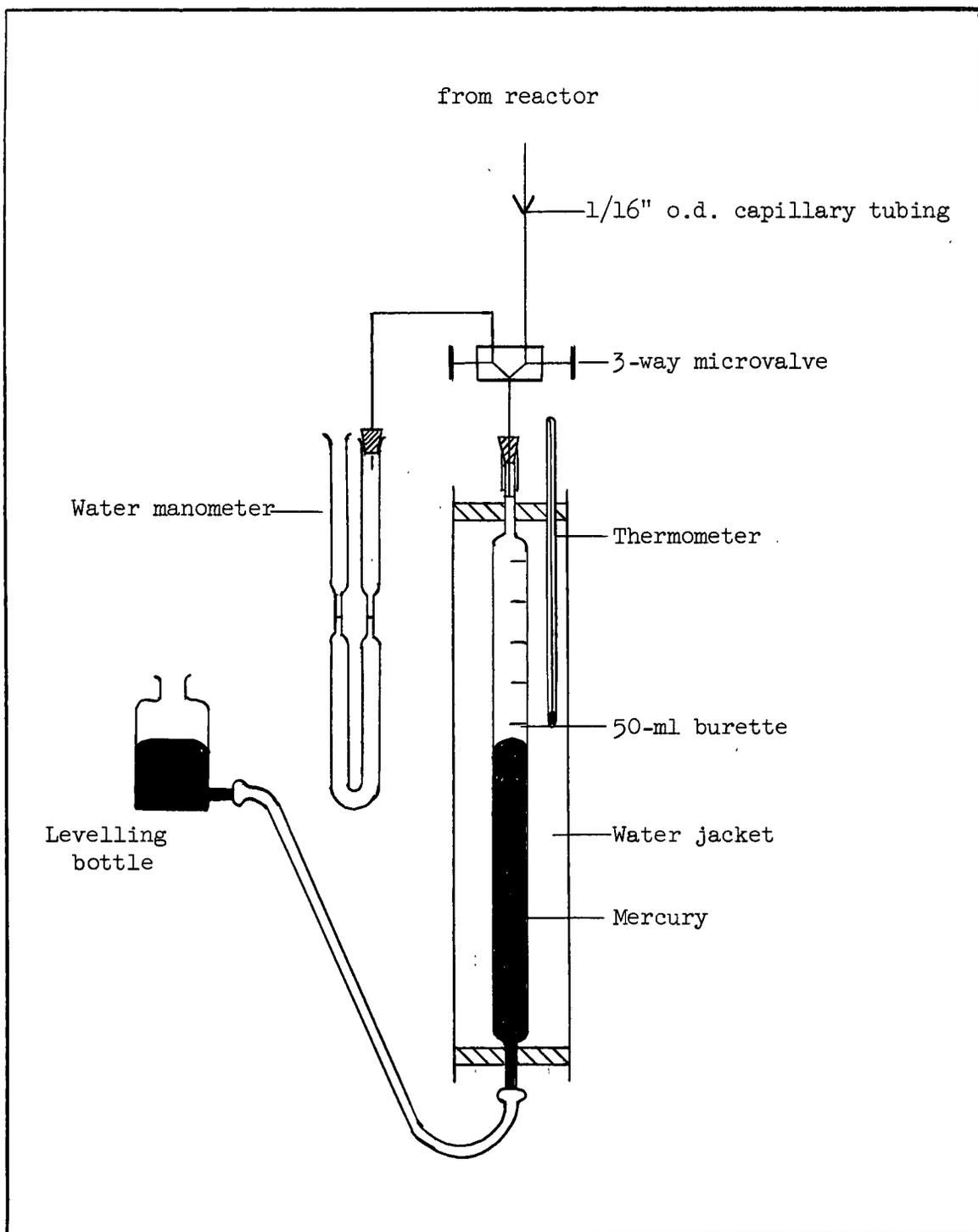


Figure B-1. Measuring Burette System for Gas Solubility Determinations

been established in the burette the volumes of liquid and gas were measured at the temperature of the water jacket and at atmospheric pressure as determined by balancing the two legs of a water manometer. Several samples could be drawn from a single charge.

Corrections were made for the residual amount of gas remaining in the burette solution and for the vapour pressure of water both in the burette and the reactor. The pressure in the reactor system was measured with a Consolidated Electrodynamics 0-1000 psig pressure transducer (Type 4-311).

The carbon monoxide was c.p. reagent grade (99.5% min) supplied by the Matheson Co. and was used without further purification. Hydrogen was of commercial grade (99.8% min) supplied by the Canadian Liquid Air Co. and was used without further purification. Degassed distilled water was used in all determinations.

## Results

### (a) Solubility of CO in Water

Data obtained for the solubility of CO in water at 25 atm from room temperature to 220°C are summarized in Table B-I and shown in Figure B-2. Published data available to 100°C at atmospheric pressure (52) when extrapolated to 25 atm agree with the present measurements to about 50°C. At higher temperatures the published values are too low by about 4% at 75°C and about 8% at 100°C.

The solubility coefficient of CO in water passes through a minimum between 50° and 100°C, a characteristic exhibited by other permanent gases (54).

The effect on the CO solubility of pressure to 65 atm at 41.5°C and to 40 atm at 140°C is summarized in Table B-II. Deviations from Henry's law

TABLE B-I

Solubility\* of CO in Water at 25 Atmospheres

Temp °C	P <sub>CO</sub> atm	S mls/g	S <sub>25</sub> mls/g	α x 10 <sup>4</sup> M/atm
24.4	25.2	.567	.561	10.00
24.4	25.2	.568	.564	10.05
24.6	25.5	.565	.554	9.87
24.9	25.6	.560	.548	9.76
25.4	25.4	.532	.524	9.34
26.1	25.6	.559	.545	9.71
26.2	25.4	.562	.552	9.84
26.4	24.9	.528	.530	9.43
27.1	24.7	.522	.529	9.43
41.5	21.4	.390	.455	8.10
41.5	27.2	.489	.450	8.02
76.5	25.9	.387	.383	6.82
100	24.8	.403	.406	7.24
100	25.0	.394	.394	7.01
120	25.0	.431	.431	7.67
120	25.1	.425	.424	7.55
140	24.6	.475	.484	8.61
140	25.4	.480	.472	8.40
140	27.0	.522	.484	8.64
140	27.5	.516	.470	8.36
160	24.5	.545	.555	9.89
160	24.8	.545	.548	9.76
180	24.1	.624	.647	11.5
180	25.1	.638	.635	11.3
200	23.4	.718	.768	13.7
200	24.2	.731	.757	13.5
220	25.5	.940	.920	16.4
220	25.9	.928	.898	16.0
220	26.2	.909	.869	15.5
220	26.5	.981	.924	16.5
220	26.6	.907	.852	15.2
220	27.1	.983	.905	16.1

\* S = mls gas (measured at S.T.P.) per gram H<sub>2</sub>O

S<sub>25</sub> = mls gas (S.T.P.) per gram H<sub>2</sub>O corrected to 25 atm assuming Henry's law

α = moles gas per litre H<sub>2</sub>O (measured at 20°C) per atmosphere of gas  
 = S<sub>25</sub> x 1.781 x 10<sup>-3</sup> (M/atm)

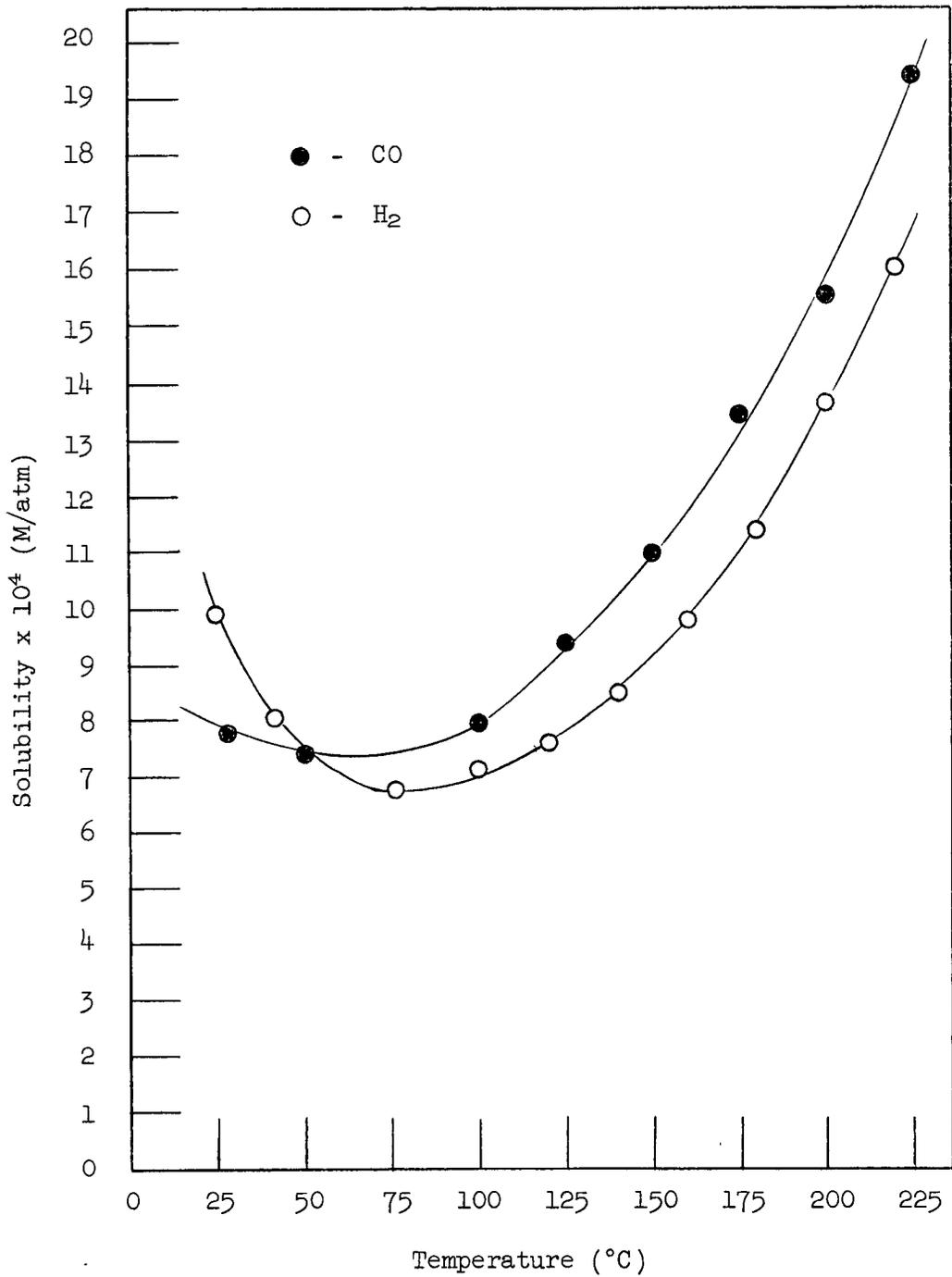


Figure B-2. Solubility of CO and H<sub>2</sub> in Water from 25 to 225°C

TABLE B- II

Effect of Pressure on Solubility\* of CO in Water

Temp °C	PCO atm	S mls/g	$\alpha \times 10^4$ M/atm
41.5	11.4	.209	8.17
	11.7	.216	8.26
	14.0	.251	7.97
	21.4	.390	8.10
	27.2	.489	8.02
	34.1	.601	7.84
	41.4	.725	7.82
	48.0	.830	7.70
	56.9	.973	7.61
	64.3	1.079	7.48
	64.3	1.096	7.59
	140	8.6	.177
13.6		.274	9.00
19.0		.367	8.59
20.7		.400	8.61
24.6		.475	8.61
25.4		.480	8.40
27.0		.522	8.64
27.5		.516	8.36
33.5		.625	8.31
34.3		.635	8.26
39.5		.727	8.21

\* S = mls. gas (measured at S.T.P.) per gram H<sub>2</sub>O

$\alpha$  = moles gas per litre H<sub>2</sub>O (measured at 20°C) per atmosphere of gas

$$= S_{25} \times 1.781 \times 10^{-3} \text{ (M/atm)}$$

were observed above about 30 atm.

### Sample Calculations

The solubility (S) in mls gas (measured at S.T.P.) per gram of water was calculated using equations B-1 and B-2. At room temperature the correction for the amount of gas remaining in solution in the burette was made on the basis of Henry's law by subtracting the partial pressure of the gas in the burette from the experimental reactor gas pressure. At higher temperatures the correction was made by adding the volume of gas remaining in the burette solution, as estimated from room temperature solubility data, to the measured gas volume. The two methods give identical results and were used in their respective temperature regions merely to facilitate computation of the data. The reproducibility of duplicate determinations was better than the estimated maximum possible error of 3 to 5% for both CO and H<sub>2</sub> measurements.

(i) At room temperature:

$$S = \left( \frac{V_g}{d \cdot V_w} \right) \left( \frac{P - P_w}{760} \right) \left( \frac{273}{T + 273} \right) \quad (B-1)$$

where T = temperature of water jacket (°C)

P = atmospheric pressure (mm Hg)

P<sub>w</sub> = vapour pressure of water (mm Hg) at T

V<sub>g</sub> = gas volume (mls) at T and P

V<sub>w</sub> = water volume (mls) at T

d = density of water at T

S = gas solubility mls (S.T.P.) per g water at the experimental temperature (T<sub>a</sub>) and pressure (P<sub>a</sub>) reduced by the partial pressure of gas in the burette.

Example: Solubility of Carbon Monoxide in Water at  $24.9 \pm 0.3^\circ\text{C}$  ( $T_a$ )

$$\begin{aligned} V_g &= 15.1 \pm 0.1 \text{ mls} & d &= 0.9977 \text{ g/ml} \\ V_w &= 24.4 \pm 0.1 \text{ mls} & P &= 762.0 \pm 0.5 \text{ mm} \\ T &= 22.2 \pm 0.1^\circ\text{C} & P_w &= 20.1 \pm 0.2 \text{ mm} \end{aligned}$$

$$\text{Measured CO pressure } (P_a) = 26.6 \pm 0.5 \text{ atm}$$

$$\text{Corrected CO pressure} = 26.6 - \frac{762.0 - 20.1}{760} = 25.6 \text{ atm}$$

$$\begin{aligned} S &= \left( \frac{15.1}{24.4 \times 0.9977} \right) \left( \frac{762.0 - 20.1}{760} \right) \left( \frac{273}{22.2 + 273} \right) \\ &= 0.560 \text{ mls CO (S.T.P.) per g water at 25.6 atm CO} \end{aligned}$$

$$\begin{aligned} \text{Possible error} &= \left( \frac{\Delta V_g}{V_g} + \frac{\Delta V_w}{V_w} + \frac{\Delta(P - P_w)}{P - P_w} + \frac{\Delta T}{T + 273} + \frac{\Delta P_a}{P_a} + \frac{\Delta T_a}{T_a + 273} \right) \\ &= \left( \frac{0.1}{15.1} + \frac{0.1}{24.4} + \frac{0.7}{741.9} + \frac{0.1}{295.2} + \frac{0.5}{26.6} + \frac{0.3}{279.9} \right) 100 \\ &= 3.1\% \end{aligned}$$

(ii) At elevated temperature:

$$S = \left( \frac{V_g + S_1 \cdot d \cdot V_w (T + 273)/273}{d \cdot V_w} \right) \left( \frac{P - P_w}{760} \right) \left( \frac{273}{T + 273} \right) \quad (\text{B-2})$$

where  $T$ ,  $P$ ,  $P_w$ ,  $V_g$ ,  $V_w$  and  $d$  have the same meaning as previously

and  $S_1$  = gas solubility mls (S.T.P.) per g water at  $T$  and 1 atm

$S$  = gas solubility mls (S.T.P.) per g water at experimental temperature ( $T_a$ ) and pressure ( $P_a$ )

Example: Solubility of carbon monoxide in water at  $200.0 \pm 0.3^\circ\text{C}$  ( $T_a$ )

$$\begin{aligned} V_g &= 12.5 \pm 0.1 \text{ mls} & d &= 0.9970 \text{ g/ml} \\ V_w &= 15.8 \pm 0.1 \text{ mls} & P &= 752.8 \pm 0.5 \text{ mm} \\ S_1 &= 0.0214 \text{ mls (S.T.P.)}/\text{g} & P_w &= 24.0 \pm 0.2 \text{ mm} \\ \text{Measured CO pressure } (P_a) &= 23.4 \pm 0.7 \text{ atm} \end{aligned}$$

$$S = \left( \frac{12.5 + (0.0214)(0.9970)(15.8)(298.2/273)}{15.8 \times 0.9970} \right) \left( \frac{752.8 - 24.0}{760} \right) \left( \frac{273}{298.2} \right)$$

$$= 0.718 \text{ mls (S.T.P.) per g water at } 23.4 \text{ atm CO}$$

$$\text{Possible error} = \left( \frac{\Delta V_g}{V_g} + \frac{\Delta V_w}{V_w} + \frac{\Delta(P - P_w)}{P - P_w} + \frac{\Delta T}{T + 273} + \frac{\Delta P_a}{P_a} + \frac{\Delta T_a}{T_a + 273} \right)$$

$$= \left( \frac{0.1}{12.5} + \frac{0.1}{15.8} + \frac{0.7}{728.8} + \frac{0.1}{298.2} + \frac{0.7}{23.4} + \frac{0.3}{473} \right) 100$$

$$= 4.7\%$$

### (b) Solubility of H<sub>2</sub> in Water

Data obtained for the solubility of H<sub>2</sub> in water at 25 atm from room temperature to 225°C are summarized in Table B-III and shown in Figure B-2. These results are in excellent agreement with other published values (55,56, 57).

Figure B-2 indicates that CO and H<sub>2</sub> are equally soluble in water at about 50°C. At higher temperatures H<sub>2</sub> is the more soluble while at lower temperatures the reverse is true.

The solubility of H<sub>2</sub> in water obeys Henry's law to about 100 atm (55).

### (c) Solubility of CO<sub>2</sub> in Water and Acetate Solutions

The solubility of CO<sub>2</sub> in water and acetate solutions was determined at 90°C from the observed pressure drop due to CO<sub>2</sub> saturation of a measured quantity of solution in the reactor. The results of these measurements as summarized in Table B-IV indicate that 1:1 solution mixtures of NaOAc and HOAc up to 2 M have little effect on the solubility of CO<sub>2</sub>. The value for the CO<sub>2</sub> solubility obtained in this way agrees with a value interpolated from published data (58) at 25 atm, if a 10% deviation from Henry's law is assumed. Other published data at 15°C (59) indicate that such a deviation is reasonable.

TABLE B-III

Solubility\* of H<sub>2</sub> in Water

Temp °C	P <sub>CO</sub> atm	S mls/g	S <sub>25</sub> mls/g	$\alpha \times 10^4$ M/atm
28.1	24.9	.434	.435	7.75
28.1	25.2	.438	.434	7.73
28.2	25.4	.447	.440	7.84
50	24.7	.414	.420	7.47
50	24.6	.414	.421	7.49
50	24.6	.402	.409	7.28
100	24.3	.440	.452	8.05
100	24.4	.445	.456	8.12
100	24.8	.444	.448	7.97
125	25.3	.535	.529	9.41
125	25.9	.547	.528	9.40
125	26.4	.551	.521	9.28
125	25.8	.542	.526	9.38
150	25.7	.626	.609	10.8
150	25.8	.634	.616	11.0
150	24.8	.615	.619	11.0
175	24.6	.742	.753	13.4
175	25.1	.743	.739	13.2
200	25.8	.900	.871	15.5
200	25.5	.908	.889	15.8
225	25.3	1.101	1.089	19.4
225	24.9	1.075	1.081	19.3

\* S = mls/gas (measured at S.T.P.) per gram H<sub>2</sub>O

S<sub>25</sub> = mls gas (S.T.P.) per gram H<sub>2</sub>O corrected to 25 atm assuming Henry's law

$\alpha$  = moles gas per litre H<sub>2</sub>O (measured at 20°C) per atmosphere of gas

= S<sub>25</sub> x 1.781 x 10<sup>-3</sup> (M/atm)

TABLE B-IV

Solubility\* of CO<sub>2</sub> in Acetate Solutions at 90°C

[NaOAc] M	[HOAc] M	P <sub>CO<sub>2</sub></sub> atm	S mls/g	S <sub>1</sub> mls/g	α x 10 <sup>2</sup> M/atm
--	--	2.61	.605	.232	1.02
--	--	2.66	.627	.236	1.05
0.2	0.2	2.57	.606	.236	1.05
0.2	0.2	2.60	.614	.236	1.05
2.0	2.0	2.56	.604	.238	1.06

\* S = mls gas (measured at S.T.P.) per gram solution

S<sub>1</sub> = mls gas (S.T.P.) per gram solution corrected to one atmosphere assuming Henry's law

α = moles gas per litre of solution (measured at 20°C) per atmosphere

$$= S_1 \times 4.454 \times 10^{-2} \text{ (M/atm)}$$

The measured absorption coefficient for CO<sub>2</sub> at 90°C together with other data for the solubility of CO<sub>2</sub> in water at one atmosphere and temperatures to 60°C as included in a recent review (53) are summarized in Table B-V and are shown in Figure B-3.

TABLE B-V

Solubility of CO<sub>2</sub> in Water at One Atmosphere

Temp °C	CO <sub>2</sub> Solubility	
	g/100 g *	$\alpha \times 10^2$ ** M/atm
20	.172	3.91
25	.149	3.38
30	.131	2.97
40	.105	2.38
50	.087	1.98
60	.072	1.64
90	--	1.05

\* CO<sub>2</sub> solubility in grams CO<sub>2</sub> per 100 g H<sub>2</sub>O from reference 53

\*\*  $\alpha$  = moles gas per litre H<sub>2</sub>O (measured at 20°C) per atmosphere of gas

$$= 0.227(\text{g CO}_2/100 \text{ g H}_2\text{O})$$

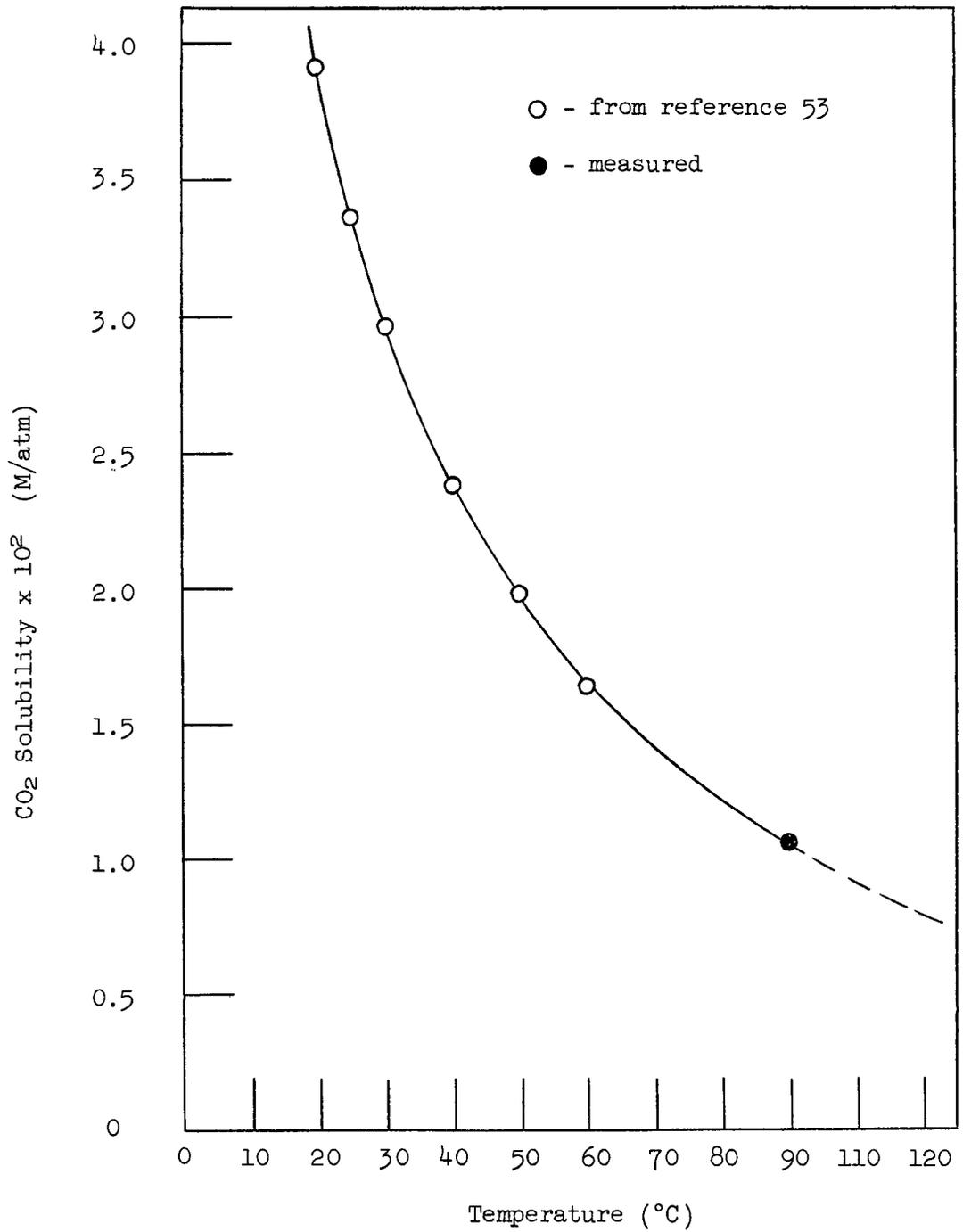
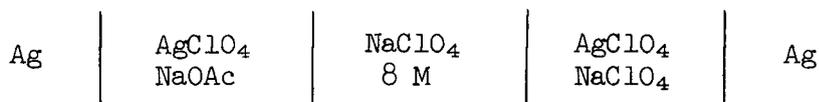


Figure B-3. Solubility of CO<sub>2</sub> in Water at One Atmosphere

APPENDIX C

SILVER-ACETATE COMPLEXING FROM E.M.F. MEASUREMENTS

Equilibria in silver acetate solutions have been extensively studied at room temperature by solubility measurements (45,60,61,62,63,64,65) and by E.M.F. measurements (39,44,66). The effect of temperatures to 90°C on silver-acetate complexing at ionic strengths between 0.1 and 0.9 has been estimated during the present investigation from E.M.F. measurements on cells of the type:



Experimental

All cell solutions contained 0.0104 M AgClO<sub>4</sub> and appropriate amounts of either NaOAc or NaClO<sub>4</sub> in equal concentrations to maintain constant ionic strength in both sides of each cell.

Silver foil electrodes, approximately 4 x 4-cm with a 5-cm lug, were conditioned by electrolyzing approximately M AgClO<sub>4</sub> solution acidified with HClO<sub>4</sub>. Each electrode was first treated as an anode to expose a fresh surface and then as a cathode to produce a coherent silver deposit. Current densities of about 0.05 amps/cm<sup>2</sup> gave suitable deposits within one to two minutes. The electrolysis conditions were not critical. The electrodes were then formed into cylindrical shapes, washed and stored in acidified distilled water until required.

The experimental cell, depicted in Figure C-1, consisted of two 22-mm i.d. pyrex solution compartments joined by about 15 cm of 6-mm i.d.

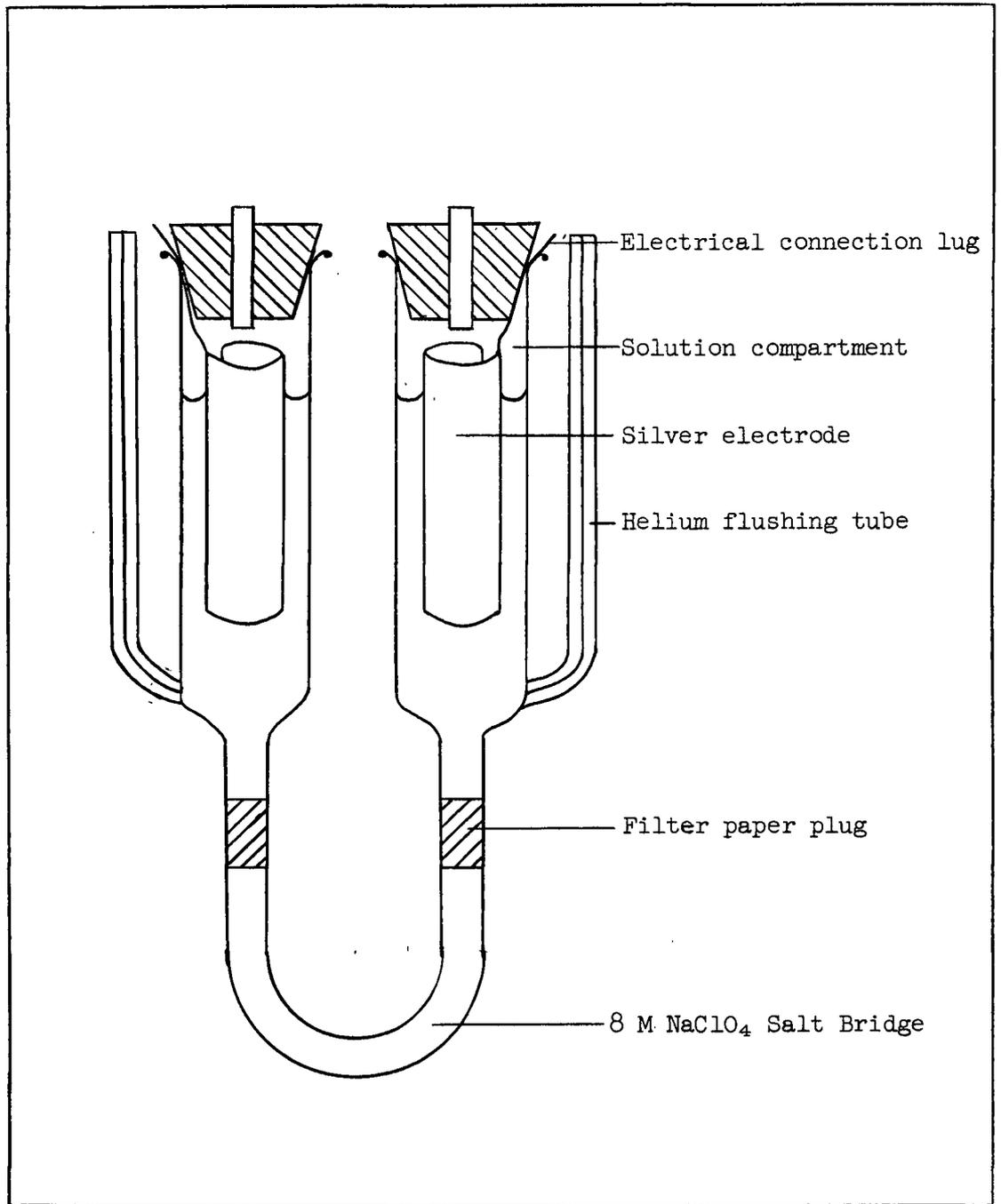


Figure C-1. Experimental Cell for E.M.F. Measurements  
(approximately half-scale)

pyrex tubing and had a total volume of about 75 mls. A capillary tube for gas flushing was attached near the bottom of each solution compartment. Filter paper plugs were used to separate the 8 M  $\text{NaClO}_4$  salt-bridge from each compartment and solution contact was made in the plugs. The cell was about 80% immersed in a stirred, electrically heated two-litre bath of ethylene glycol. The temperature was controlled to  $\pm 0.1^\circ\text{C}$  using a Yellow Springs Instrument Co. Thermistemp Temperature Controller (Model 71) with a stainless steel-clad thermister probe (No. 406). E.M.F. measurements were made with a high precision Leeds and Northrup potentiometer (No. 7552).

The general procedure consisted of pipetting sufficient 8 M  $\text{NaClO}_4$  (previously prepared with degassed distilled water and stored in a stoppered flask) to bring the solution level in the salt bridge tubing to within about two cm of the bottom of each solution compartment. After the filter paper plugs were inserted approximately 25 mls of experimental solution were added to each solution compartment and the electrodes secured 4 to 5 cm above the plugs with rubber bungs. The vessel was mounted in the glycol bath at room temperature and the solution compartments were flushed with a slow flow of helium for about five minutes. After flushing the gas outlet lines were clamped and a slight positive pressure of helium maintained over the solutions.

At room temperature the E.M.F. became constant within 2 to 4 hours and showed little deviation for periods up to 12 hours. After the room temperature value had been determined the glycol bath was heated and the E.M.F. measured at successively higher temperatures, sufficient time being allowed to attain equilibrium as evidenced by constant cell-voltage readings. The E.M.F. of cells allowed to cool from higher temperatures overnight generally reproduced the room temperature value within 10%.

## Results

The following assumptions are made:

1. The difference in liquid junction potentials is negligible.
2. Activity coefficients of  $\text{Ag}^+$  are equal in all solutions of equal ionic strength.
3.  $\text{AgClO}_4$ ,  $\text{NaClO}_4$  and  $\text{NaOAc}$  are completely dissociated.
4. The average silver-acetate complex is represented by the formula  $\overline{\text{AgOAc}}$ .

On this basis the E.M.F. of each cell, using the International or Stockholm sign convention (9), is given by:

$$E = \frac{2.30 RT}{nF} \log \frac{0.0104}{[\text{Ag}^+]} \quad (\text{C-1})$$

where  $E$  = cell E.M.F. (volts)

$R$  = universal gas constant ( $1.987 \text{ cal mole}^{-1} \text{ deg}^{-1}$ )

$F$  = Faraday constant ( $23.06 \text{ kcal/equivalent}$ )

$T$  = absolute temperature ( $^{\circ}\text{K}$ )

$n$  = number of volt equivalents (= unity)

$[\text{Ag}^+]$  = silver ion concentration in the acetate solution compartment (M)

0.0104 = silver ion concentration in the perchlorate solution compartment (M)

The concentration ratio ( $K_a$ ) for the formation of  $\overline{\text{AgOAc}}$  is given by:

$$K_a = \frac{[\overline{\text{AgOAc}}]}{[\text{Ag}^+][\text{OAc}^-]} \quad (\text{M}^{-1}) \quad (\text{C-2})$$

The results of measurements made on six cells are summarized in Table C-I.  $K_a$  estimated using equations C-1 and C-2 is essentially independent of ionic strength between 0.1 and 0.9 and temperatures to  $90^{\circ}\text{C}$  and has an average value of  $3.7 \pm 0.7 \text{ M}^{-1}$ .

TABLE C-I

Effect of Temperature on Silver-Acetate Complexing

Using 0.0104 M AgClO<sub>4</sub>

Cell No	[NaOAc] M	Temp °C	EMF mv	[Ag <sup>+</sup> ] M	K <sub>a</sub> * M <sup>-1</sup>
1	.10	23	9.0 ± 1.0	.0073	4.4
2	.20	24	12.0 ± 1.0	.0065	3.1
	.20	25	12.5 ± 1.0	.0064	3.2
	.20	50	15.0 ± 1.0	.0061	3.6
	.20	90	17.0 ± 1.5	.0060	3.7
3	.50	25	27.0 ± 1.0	.0036	3.8
	.50	35	29.0 ± 1.5	.0035	4.0
	.50	50	31.5 ± 1.5	.0034	4.2
4	.50	23	24.0 ± 1.0	.0041	3.1
5	.50	24	23.5 ± 1.0	.0042	3.0
	.50	25	26.0 ± 1.0	.0038	3.5
	.50	90	33.5 ± 1.5	.0037	3.7
6	.90	24	35.0 ± 1.0	.0027	3.2
	.90	35	39.0 ± 1.0	.0024	3.7
	.90	50	45.0 ± 1.5	.0021	4.4
	.90	90	50.0 ± 2.0	.0021	4.4

$$* K_a = \frac{0.0104 - [Ag^+]}{[Ag^+]( [NaOAc] - [Ag^+] )}$$

APPENDIX D

SUMMARY OF SELECTED EXPERIMENTAL DATA FOR THE REDUCTION OF  
SILVER(I) SOLUTIONS BY CARBON MONOXIDE

I. EFFECT OF CO PRESSURE AT 90°C (Figure 5)

(a) Initial Conditions: 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc; 0.078 M HOAc

Expt No	P <sub>CO</sub> atm	R* x 10 <sup>6</sup> M s <sup>-1</sup>	R <sup>**</sup> x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
234	1.67	7.2	4.31
233	1.69	5.0	2.96
231	3.10	13.6	4.39
232	4.17	20.0	4.79
214	5.17	27.1	5.24
230	5.22	23.7	4.35
207	5.24	23.7	4.34
236	9.28	42.0	4.57
235	12.8	43.3	3.38
237	13.3	54.4	4.09
238	29.8	132.	4.43

(b) Initial Conditions: 0.115 M AgClO<sub>4</sub>; 0.045 M NaOAc; 0.766 M HOAc

Expt No	P <sub>CO</sub> atm	R* x 10 <sup>6</sup> M s <sup>-1</sup>	R <sup>**</sup> x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
162	11.4	5.8	.509
163	19.4	10.0	.515
165 <sup>a</sup>	25.6	12.7	.496
164 <sup>b</sup>	27.5	14.2	.516
161	27.7	14.4	.520

- a - Reactor thoroughly cleaned with HNO<sub>3</sub> prior to charging.  
b - Contained 0.1g Ag precipitated in previous experiment plus 2.0 g silver sponge obtained from Consolidated Mining and Smelting Co. Ltd.

\* R = -d[CO]/dt  
\*\* R' = R/P<sub>CO</sub>

II. EFFECT OF ACETIC ACID AT 90°C (Figure 6)

Initial Conditions: 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc

Expt No	[HOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	PCO atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
209	.585	1.7	5.17	1.52
212	.585	1.7	5.24	1.84
208	.160	6.3	5.31	3.61
210	.160	6.3	5.31	3.89
238	.0978	10.2	29.8	4.43
237	.0898	11.1	13.3	4.09
235	.0886	11.3	12.8	3.39
236	.0868	11.5	9.28	4.53
230	.0832	12.0	5.22	4.54
207	.0830	12.0	5.24	4.34
214	.0828	12.1	5.17	5.24
232	.0818	12.2	4.17	4.79
231	.0805	12.4	3.10	4.39
233	.0786	12.7	1.69	2.96
234	.0786	12.7	1.67	4.31
213	.0624	16.0	5.24	6.88
206	.0460	21.7	5.17	7.73
211	.0334	29.9	5.17	10.1

III. EFFECT OF SILVER-ACETATE COMPLEXING AT 90°C (Figures 6, 7, 8; TableIV)

A. Initial Conditions: 0.050 M AgClO<sub>4</sub>; 0.045 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	PCO atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
A-180	.048	.043	4.4	28.0	.152
A-181	.042	.037	18.9	27.9	.559
A-191	.046	.041	10.6	28.1	.418
A-192	.046	.041	5.4	28.1	.304
A-193	.049	.043	1.2	27.8	.106
Average:	.048	.041			
$I' = 0.15 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.017 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

B. Initial Conditions: 0.100 M  $\text{AgClO}_4$ ; 0.045 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
B-142	.097	.042	4.39	27.2	.420
B-149	.096	.041	4.36	27.6	.368
B-152	.096	.041	1.30	27.6	.368
B-153	.095	.040	1.30	27.7	.347
Average:	.096	.041			
$I' = 0.31 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.026 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

C. Initial Conditions: 0.047 M  $\text{AgClO}_4$ ; 0.090 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
C-308	.046	.090	.64	12.4	.230
C-307	.045	.089	4.41	12.2	.504
C-306	.044	.087	10.7	12.1	.853
Average:	.045	.089			
$I' = 0.22 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.058 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

D. Initial Conditions: 0.117 M  $\text{AgClO}_4$ ; 0.045 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
D-299	.116	.044	.63	12.1	.352
D-298	.115	.043	4.41	12.1	.619
D-297	.114	.042	10.7	12.4	1.00
Average:	.115	.043			
$I' = 0.32 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.066 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

E. Initial Conditions: 0.100 M AgClO<sub>4</sub>; 0.090 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
E-139	.094	.084	5.38	26.6	.804
E-140	.094	.084	5.38	26.7	.755
E-141	.089	.079	5.24	26.3	.711
E-151	.095	.085	2.20	27.4	.566
Average:	.090	.080			
$I' = 0.40 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.074 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

F. Initial Conditions: 0.047 M AgClO<sub>4</sub>; 0.180 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
F-305	.045	.179	.63	12.2	.467
F-304	.044	.177	4.39	12.3	.799
F-303	.043	.176	10.6	12.2	1.27
Average:	.044	.178			
$I' = 0.43 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.081 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

G. Initial Conditions: 0.050 M AgClO<sub>4</sub>; 0.225 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
G-135	.033	.208	16.1	27.4	1.73
G-182	.041	.215	4.3	28.2	.701
G-189	.044	.219	2.1	27.7	.549
G-190	.043	.218	1.6	28.4	.602
Average:	.042	.215			
$I' = 0.43 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.077 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

H. Initial Conditions: 0.235 M AgClO<sub>4</sub>; 0.045 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
H-293	.233	.043	.63	11.6	.56
H-292	.231	.041	4.37	11.8	1.21
H-291	.229	.039	10.4	11.5	1.83
Average:	.230	.041			
$I' = 0.50 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.133 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

I. Initial Conditions: 0.117 M AgClO<sub>4</sub>; 0.090 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
I-296	.115	.088	.63	11.8	.56
I-295	.114	.087	4.37	12.0	1.11
I-294	.110	.083	10.2	12.2	2.32
Average:	.114	.087			
$I' = 0.44 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.178 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

J. Initial Conditions: 0.235 M AgClO<sub>4</sub>; 0.090 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
J-290	.231	.087	.62	11.6	1.02
J-283	.230	.085	1.26	11.9	1.34
J-289	.227	.082	4.30	11.9	2.43
J-285	.221	.076	9.60	11.6	4.47
Average:	.225	.082			
$I' = 0.78 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.384 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

K. Initial Conditions: 0.117 M AgClO<sub>4</sub>; 0.180 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
K-302	.114	.177	.63	12.1	.92
K-301	.111	.174	4.32	12.0	2.06
K-300	.105	.168	9.76	11.7	3.87
Average:	.110	.173			
$I' = 0.70 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.322 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

L. Initial Conditions: 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
L-209	.113	.193	1.7	5.17	1.52
L-212	.113	.193	1.7	5.24	1.84
L-208	.111	.191	6.3	5.31	3.61
L-210	.111	.191	6.3	5.31	3.89
L-238	.096	.175	10.2	29.8	4.43
L-237	.103	.183	11.1	13.3	4.09
L-235	.104	.184	11.3	12.8	3.39
L-236	.106	.186	11.5	9.28	4.53
L-230	.110	.190	12.0	5.22	4.54
L-207	.110	.190	12.0	5.24	4.34
L-214	.110	.190	12.1	5.17	5.24
L-232	.111	.191	12.2	4.17	4.79
L-231	.112	.192	12.4	3.10	4.39
L-233	.114	.194	12.7	1.69	2.96
L-234	.114	.194	12.7	1.67	4.31
L-213	.108	.188	16.0	5.24	6.88
L-206	.108	.188	21.7	5.17	7.73
L-211	.105	.185	29.9	5.17	10.1
Average:	.110	.190			
$I' = 0.90 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.32 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

M. Initial Conditions: 0.047 M AgClO<sub>4</sub>; 0.676 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
M-311	.043	.672	.63	12.1	1.04
M-310	.039	.670	4.32	12.4	1.94
M-309	.036	.665	9.87	12.4	3.34
Average:	.040	.670			
$I' = 0.87 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.249 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

N. Initial Conditions: 0.058 M AgClO<sub>4</sub>; 0.556 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M, a <sup>-1</sup> , s <sup>-1</sup>
N-254	.057	.555	.51	5.31	1.00
N-255	.056	.554	2.57	5.44	1.58
N-256	.055	.553	8.78	5.37	3.24
Average:	.056	.554			
$I' = 0.85 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.275 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

O. Initial Conditions: 0.058 M AgClO<sub>4</sub>; 0.778 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
O-250	.057	.777	.52	5.24	1.24
O-252	.057	.777	1.03	5.37	1.58
O-251	.056	.776	2.57	5.31	1.95
O-253	.056	.776	5.10	5.31	2.92
O-249	.055	.775	8.76	5.37	3.92
Average:	.056	.776			
$I' = 1.10 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.340 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

IV. REACTION RATES USED IN EXTRAPOLATION TO ZERO ACETATE AT 90°C  
(Figures 20, 21, 22; Table VI)

P. Initial Conditions: 0.050 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 1

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
P-184	.043	.262	.278	28.2	.0201	.245	.777	10.8
P-182	.041	.215	.235	28.2	.0173	.198	.702	9.53
P-185	.043	.172	.188	28.2	.0156	.156	.759	9.15
P-183	.041	.126	.144	27.9	.0123	.114	.671	7.85
P-186	.044	.083	.097	28.0	.0094	.074	.650	6.71
P-181	.042	.037	.053	27.9	.0046	.032	.476	5.54

$$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 4.6 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$$

Q. Initial Conditions: 0.100 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 1

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
Q-137	.082	.207	.243	26.4	.0322	.175	1.73	13.1
Q-138	.085	.165	.195	26.4	.0285	.137	1.53	10.5
Q-136	.085	.120	.150	26.5	.0225	.098	1.58	10.5

$$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 6.8 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$$

R. Initial Conditions: 0.123 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 1

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
R-287	.115	.087	.102	12.7	.0223	.065	2.48	11.4
R-288	.118	.017	.029	12.8	.0051	.012	1.75	10.0

$$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 9.6 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$$

S. Initial Conditions: 0.235 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 1

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
S-285	.223	.076	.104	11.6	.0313	.045	4.47	14.9
S-286	.226	.013	.032	11.9	.0059	.007	2.59	14.0
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 13.7 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

T. Initial Conditions: 0.100 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 5

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
T-150	.094	.129	.681	27.5	.0259	.103	.611	16.0
T-154	.095	.108	.569	27.5	.0228	.085	.575	14.4
T-151	.095	.085	.455	27.4	.0187	.066	.555	13.5
T-149	.096	.041	.229	27.6	.0099	.031	.368	8.5
T-142	.097	.042	.228	27.2	.0102	.032	.419	9.4
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 6.0 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

U. Initial Conditions: 0.064 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 8.7

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
U-276	.063	.090	.785	4.83	.0139	.076	.570	32.2
U-277	.063	.063	.393	4.90	.0078	.038	.354	18.0
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 4.4 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

V. Initial Conditions: 0.130 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 8.7

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
V-281	.126	.146	1.314	12.1	.0362	.110	1.19	43.3
V-280	.127	.022	.221	12.3	.0066	.015	.649	21.8
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 18.0 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

W. Initial Conditions: 0.163 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 8.7

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
W-278	.161	.073	.655	4.94	.0246	.049	1.13	30.1
W-279	.162	.024	.219	4.68	.0087	.015	.908	22.9
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 19.4 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

X. Initial Conditions: 0.235 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 8.7

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
X-283	.230	.085	.793	11.9	.0355	.050	1.34	29.9
X-282	.232	.042	.399	11.8	.0184	.024	.903	19.6
X-284	.232	.033	.319	12.1	.0146	.018	.890	19.4
$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_0 = 12.8 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$								

Y. Initial Conditions: 0.270 M AgClO<sub>4</sub>; [HOAc]/[NaOAc] = 8.7

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	[AgOAc] M	[OAc <sup>-</sup> ] M	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>	R' $\frac{[\text{HOAc}]}{[\text{AgOAc}]}$ x 10 <sup>6</sup> M s <sup>-1</sup> a <sup>-1</sup>
Y-270	.267	.092	.829	5.05	.0419	.050	2.27	45.1
Y-274	.268	.046	.415	4.88	.0218	.024	1.55	29.5
Y-273	.269	.018	.167	4.92	.0087	.009	1.18	22.8
Y-272	.268	.0083	.084	4.97	.0041	.004	.969	19.8

$$\left( R' \frac{[\text{HOAc}]}{[\text{AgOAc}]} \right)_o = 18.4 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$$

V. PH\* CHANGES DURING REDUCTION OF UNBUFFERED AgClO<sub>4</sub> SOLUTIONS AT 90°C AND 53 ATM CO (Figures 23 and 24; Tables VII and VIII)

Experiment No. 262

Time sec	[Ag <sup>+</sup> ] M	pH	[H <sup>+</sup> ] x 10 <sup>3</sup> M	log t
0	.0530	~ 5.2	~ 0.007	--
180		3.15	0.7	2.26
390		2.92	1.2	2.59
780		2.71	2.0	2.89
1,800		2.55	2.8	3.26
3,600		2.32	4.7	3.56
6,300		2.27	5.4	3.80
9,000		2.14	7.2	3.96
12,780	.0458	2.09	8.1	4.11

\* The pH is defined in terms of hydrogen ion concentration rather than activity since the pH-meter was calibrated against mixtures of standard HClO<sub>4</sub> and AgClO<sub>4</sub> solutions.

Experiment No. 260

Time sec	[Ag <sup>+</sup> ] M	pH	[H <sup>+</sup> ] x 10 <sup>3</sup> M	log t
0	.104	~ 5.0	~ 0.01	--
120		3.05	0.9	2.08
240		2.77	1.7	2.38
480		2.61	2.5	2.68
990		2.41	3.9	3.00
1,920		2.26	5.5	3.28
4,740		2.05	8.9	3.68
10,000	.090	1.87	13.5	4.00

Experiment No. 261

Time sec	[Ag <sup>+</sup> ] M	pH	[H <sup>+</sup> ] x 10 <sup>3</sup> M	log t
0	.211	~ 4.5	~ 0.03	--
180		2.62	2.4	2.26
300		2.51	3.1	2.48
525		2.30	5.0	2.72
1,020		2.14	7.3	3.01
1,810		1.96	11.0	3.26
3,600		1.80	15.9	3.56
6,310		1.67	22.4	3.80
9,000		1.63	23.4	3.96
11,700	.179	1.47	33.9	4.07

Experiment No. 263

Time sec	[Ag <sup>+</sup> ] M	pH	[H <sup>+</sup> ] x 10 <sup>3</sup> M	log t
0	1.06	~ 4.0	~ 0.1	--
180		1.67	21	2.26
360		1.57	27	2.56
660		1.43	37	2.82
1,140		1.30	50	3.06
2,040		1.10	79	3.31
3,840		0.95	112	3.58
5,640		0.90	126	3.75
8,340		0.83	148	3.92
11,040	.85	0.69	204	4.04

VI. EXPERIMENTAL DATA INCLUDED IN LEAST SQUARE REGRESSION ANALYSIS, SECTION III-10 (TABLE IX) BUT NOT USED IN GRAPHICAL ANALYSES, AT 90°C

(a) Initial Conditions: 0.144 M AgClO<sub>4</sub>; 0.195 M NaOAc; 0.195 M HOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
265	.142	.192	.197	5.16	3.75
264 <sup>a</sup>	.141	.191	.198	5.10	4.09
266 <sup>b</sup>	.141	.191	.197	5.04	4.02
267 <sup>c</sup>	.142	.192	.197	4.78	3.87
268 <sup>d</sup>	.142	.192	.197	5.04	3.75

a - Air evacuated from solution in reactor prior to heat-up  
 b - Added CO<sub>2</sub> to 5.7 psi prior to CO addition  
 c - Contained 3.3 g fine 316 S.S. filings  
 d - Contained 1.0 g Ag precipitated during previous experiments plus 3.0 g Ag sponge

(b) Initial Conditions: 0.111 M HOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
239	.068	.220	.113	5.22	2.22
240	.068	.330	.114	5.25	2.97
241	.070	.044	.112	5.45	.785
242	.069	.109	.113	5.17	1.57
243	.133	.043	.113	5.11	1.57
244	.132	.108	.115	5.15	3.16
245	.129	.216	.118	5.11	6.34
246	.278	.104	.118	5.10	6.53
247	.044	.110	.112	5.27	.955
248	.069	.110	.113	5.30	1.43

(c) Initial Conditions: 0.115 M AgClO<sub>4</sub>; 0.045 M NaOAc; 0.766 M HOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] M	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
162	.114	.044	.767	11.4	.509
163	.110	.040	.771	19.4	.515
165	.111	.041	.770	25.6	.496
164	.110	.040	.771	27.5	.516
161	.110	.040	.771	27.7	.520

VII. EFFECT OF TEMPERATURE (Figure 26; Table XI)

(a) Initial Conditions: 60°C, 0.100 M AgClO<sub>4</sub>; 0.135 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
223	.100	.135	1.3	5.38	.177
222	.099	.134	11.0	5.51	.468
221	.099	.134	21.5	5.30	.720
Average:	.099	.134			
$I' = 0.14 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.029 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

(b) Initial Conditions: 80°C; 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
220	.113	.193	1.7	5.41	0.93
219	.112	.192	6.3	5.47	1.79
218	.111	.192	12.4	5.48	2.64
217	.110	.191	17.2	5.38	3.43
216	.110	.190	23.2	5.43	3.95
215	.107	.187	32.6	5.41	6.76
Average:	.110	.191			
$I' = 0.64 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 0.165 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

(c) Initial Conditions: 110°C; 0.115 M AgClO<sub>4</sub>; 0.195 M NaOAc

Expt No	[Ag(I)] M	[NaOAc] M	[HOAc] <sup>-1</sup> M <sup>-1</sup>	P <sub>CO</sub> atm	R' x 10 <sup>6</sup> M a <sup>-1</sup> s <sup>-1</sup>
205	.112	.192	1.7	4.56	5.01
199	.109	.189	6.2	4.56	9.72
204	.105	.186	11.6	4.56	15.6
203	.103	.183	20.0	4.49	20.9
202	.103	.183	20.0	4.49	20.9
197	.102	.182	19.7	4.63	21.6
201	.101	.182	27.6	4.49	23.7
200	.100	.181	27.2	4.53	24.6
198	.099	.180	26.1	4.49	27.6
Average:	.105	.185			
$I' = 3.2 \times 10^{-6} \text{ M atm}^{-1} \text{ sec}^{-1}$ $S' = 1.04 \times 10^{-6} \text{ M}^2 \text{ atm}^{-1} \text{ sec}^{-1}$					

APPENDIX E

THERMODYNAMICS OF THE OXIDATION OF CO, H<sub>2</sub>, HCOOH AND HCOO<sup>-</sup>  
 IN AQUEOUS SOLUTION AT 25°C (Figure 1)

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The thermodynamics of the reactions considered in Figure 1 (Section I-2) are summarized in terms of the free energy data (10) in Table E-I using the equations E-1 and E-2. The standard states are chosen as unit molarity for dissolved species and one atmosphere for gaseous species. The International or Stockholm Convention (9) is used for the sign of electrode potentials.

TABLE E-I

Standard Free Energy at 25°C  
 (kcal/mole)

CO(g)	-32.808
CO <sub>2</sub> (g)	-94.260
CO <sub>3</sub> <sup>=</sup> (aq)	-126.22
HCO <sub>3</sub> <sup>-</sup> (aq)	-140.31
HCOO <sup>-</sup> (aq)	-80.0
HCOOH(aq)	-85.1
H <sup>+</sup> (aq)	0.0
H <sub>2</sub> (g)	0.0
H <sub>2</sub> O(l)	-56.690

$$\Delta G^\circ = -nFE^\circ = -2.30 RT \log K \quad (\text{E-1})$$

$$E = E^\circ - \frac{2.30 RT}{nF} \log Q \quad (\text{E-2})$$

where

$\Delta G^\circ$  = standard Gibbs free energy for the electrode reaction (kcal/mole)

$E^\circ$  = standard electrode potential (volt/mole)

$E$  = electrode potential (volt/mole)

$n$  = number of volt equivalents

F = Faraday constant (23.06 kcal/equivalent)

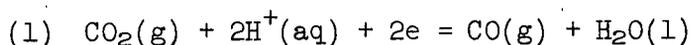
R = universal gas constant (1.987 cal mole<sup>-1</sup> deg<sup>-1</sup>)

T = absolute temperature (°K)

K = thermodynamic equilibrium constant

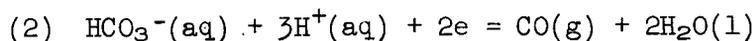
Q = activity quotient

$$\frac{2.303RT}{F} = 0.059 \text{ (volts/equivalent) at } 25^{\circ}\text{C}$$



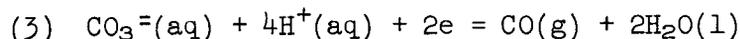
$$\Delta G^{\circ} = 4.762 \text{ kcal/mole; } E^{\circ} = 0.103 \text{ volts}$$

$$E = -0.103 - 0.059\text{pH} - 0.030 \log(a_{\text{CO}}/a_{\text{CO}_2})$$



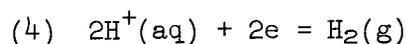
$$\Delta G^{\circ} = -5.88 \text{ kcal/mole; } E^{\circ} = 0.128 \text{ volts}$$

$$E = 0.128 - 0.089\text{pH} - 0.030 \log(a_{\text{CO}}/a_{\text{HCO}_3^-})$$



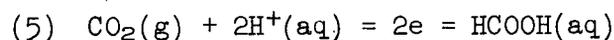
$$\Delta G^{\circ} = -19.97 \text{ kcal/mole; } E^{\circ} = 0.433 \text{ volts}$$

$$E = 0.433 - 0.118\text{pH} - 0.030 \log(a_{\text{CO}}/a_{\text{CO}_3^{2-}})$$



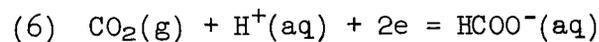
$$\Delta G^{\circ} = 0; \quad E^{\circ} = 0$$

$$E = -0.059\text{pH} - 0.030 \log(a_{\text{H}_2})$$



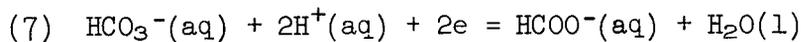
$$\Delta G^{\circ} = 9.16 \text{ kcal/mole; } E^{\circ} = -0.199 \text{ volts}$$

$$E = -0.199 - 0.059\text{pH} - 0.030 \log(a_{\text{HCOOH}}/a_{\text{CO}_2})$$



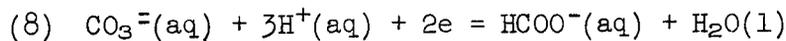
$$\Delta G^{\circ} = 14.26 \text{ kcal/mole; } E^{\circ} = -0.309 \text{ volts}$$

$$E = -0.309 - 0.030\text{pH} - 0.030 \log(a_{\text{HCOO}^-}/a_{\text{CO}_2})$$



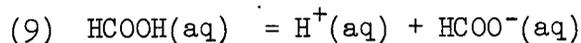
$\Delta G^\circ = 3.62 \text{ kcal/mole}; E^\circ = -0.079 \text{ volts}$

$E = -0.079 - 0.059\text{pH} - 0.030 \log(a_{\text{HCOO}^-}/a_{\text{HCO}_3^-})$



$\Delta G^\circ = -10.47 \text{ kcal/mole}; E^\circ = 0.227 \text{ volts}$

$E = 0.227 - 0.089\text{pH} - 0.030 \log(a_{\text{HCOO}^-}/a_{\text{CO}_3^{2-}})$



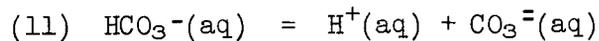
$\Delta G^\circ = 5.1 \text{ kcal/mole}; \log K = -3.7$

$\text{pH} = 3.7 + \log(a_{\text{HCOO}^-}/a_{\text{HCOOH}})$



$\Delta G^\circ = 10.64 \text{ kcal/mole}; \log K = -7.8$

$\text{pH} = 7.8 + \log(a_{\text{HCO}_3^-}/a_{\text{CO}_2})$



$\Delta G^\circ = 14.09 \text{ kcal/mole}; \log K = -10.3$

$\text{pH} = 10.3 + \log(a_{\text{CO}_3^{2-}}/a_{\text{HCO}_3^-})$

APPENDIX F

NUMERICAL INTEGRATION OF EXPERIMENTAL RATE LAW (Figure 25, Section III-10)

The rate of CO-reduction of silver perchlorate in sodium acetate - acetic acid buffered solution is given by equation 19:

$$R' = k_1' [\overline{\text{AgOAc}}] + k_2' [\text{Ag}^+]^2 \frac{[\text{OAc}^-]}{[\text{HOAc}]} + k_3' [\text{Ag}^+] [\overline{\text{AgOAc}}] \frac{[\text{OAc}^-]}{[\text{HOAc}]} \quad (19)$$

A method for numerically integrating equation 19 is outlined in the present section. From equation 19,

$$-\frac{d[\text{CO}]}{dt} = P_{\text{CO}} R' \quad (\text{M sec}^{-1}) \quad (\text{F-1})$$

From Appendix A\*:

$$-\frac{d[\text{CO}]}{dt} = \frac{dP_{\text{T}}}{dt} \left( \frac{(F + \alpha_{\text{CO}})(F + \alpha_{\text{CO}_2})}{(\alpha_{\text{CO}_2} - \alpha_{\text{CO}})} \right) (\text{M sec}^{-1}) \quad (\text{A-1})$$

$$\text{Let rate factor (R.F.)} = \frac{(F + \alpha_{\text{CO}})(F + \alpha_{\text{CO}_2})}{(\alpha_{\text{CO}_2} - \alpha_{\text{CO}})} \quad (\text{M/atm})$$

$$\therefore \frac{-dP_{\text{T}}}{dt} = \frac{P_{\text{CO}}}{\text{R.F.}} R' \quad (\text{F-2})$$

$$= \left( \frac{P_{\text{CO}}^i - \Delta P_{\text{CO}}}{\text{R.F.}} \right) R' \quad (\text{atm sec}^{-1}) \quad (\text{F-3})$$

where  $P_{\text{CO}}^i$  = initial CO pressure

and  $\Delta P_{\text{CO}}$  = decrease in CO pressure in time t

From Appendix A, the amount of CO consumed in time t is given by:

$$X = \Delta P_{\text{CO}} (F + \alpha_{\text{CO}}) = \Delta P_{\text{T}} \times \text{R.F.} \quad (\text{M}) \quad (\text{F-4})$$

---

\* See Appendix A for definition of terms.

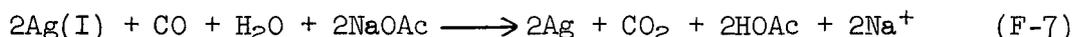
$$\therefore \Delta P_{CO} = \Delta P_T \frac{R.F.}{F + \alpha_{CO}} \quad (\text{atm}) \quad (\text{F-5})$$

Substitution in F-3 gives:

$$\frac{-dP_T}{dt} = \left( \frac{P_{CO}^i - \Delta P_T \frac{R.F.}{F + \alpha_{CO}}}{R.F.} \right) R' \quad (\text{atm sec}^{-1}) \quad (\text{F-6})$$

R.F. and  $F + \alpha_{CO}$  can be calculated by the method outlined in Appendix A.  $P_{CO}^i$  and  $\Delta P_T$  can be obtained from an experimental pressure vs time record.

R' can be evaluated in the following manner, using equation 19 and the stoichiometry of the overall reduction reaction represented by equation F-7:



Since X represents the amount of CO consumed in time t, then, if  $[ ]_i$  denotes initial concentration,

$$[\text{AgClO}_4]_i - 2X = [\overline{\text{AgOAc}}] + [\text{Ag}^+] \quad (\text{F-8})$$

$$[\text{NaOAc}]_i - 2X = [\overline{\text{AgOAc}}] + [\text{OAc}^-] \quad (\text{F-9})$$

$$[\text{HOAc}]_i + 2X = [\text{HOAc}] \quad (\text{F-10})$$

where X is given by F-4.  $[\overline{\text{AgOAc}}]$  can also be expressed in terms of the association constant,  $K_a$ , according to equation F-11:

$$[\overline{\text{AgOAc}}] = K_a [\text{Ag}^+] [\text{OAc}^-] \quad (\text{F-11})$$

Substitution for  $[\text{Ag}^+]$  and  $[\text{OAc}^-]$  from F-8 and F-9 gives:

$$[\overline{\text{AgOAc}}] = b - (b^2 - c)^{\frac{1}{2}} \quad (\text{F-12})$$

where  $b = 0.5 ([\text{AgClO}_4]_i + [\text{NaOAc}]_i + 1/K_a - 4X)$

$c = ([\text{AgClO}_4]_i [\text{NaOAc}]_i - 2X ([\text{AgClO}_4]_i + [\text{NaOAc}]_i) + 4X)$

Thus  $R'$  can be evaluated in terms of F-8, F-9, F-10 and F-12 using an experimental set of rate parameters.

All the terms on the right-hand side of F-6 are now available and F-7 can be integrated from zero to  $t$ :

$$\frac{-dP_T}{dt} = \left( \frac{P_{CO}^i - \Delta P_T R.F. / (F + \alpha_{CO})}{R.F.} \right) R' \quad (\text{atm sec}^{-1}) \quad (\text{F-6})$$

$$= 60 \times 14.7 \left( \frac{P_{CO}^i - \Delta P_T R.F. / (F + \alpha_{CO})}{R.F.} \right) R' \quad (\text{psi min}^{-1}) \quad (\text{F-13})$$

$$= f(\Delta P_T) \quad (\text{psi min}^{-1}) \quad (\text{F-14})$$

$$\int_0^t dt = t = \int_0^{\Delta P_T} (f(\Delta P_T))^{-1} dP_T \quad (\text{min}) \quad (\text{F-15})$$

The time (in min) required for a decrease in total pressure (in psi) can be calculated from the area under a  $(f(\Delta P_T))^{-1}$  vs  $\Delta P_T$  plot.

The integral in F-15 was evaluated numerically on an IBM 1620 digital computer using the trapezoidal rule at 1.0 psi intervals.

### Sample Calculations

Expt Nos 207 and 230 (Figure 25, Section III-10; see also Appendix D-III-L)

Initial Conditions: 0.115 M  $\text{AgClO}_4$ ; 0.195 M  $\text{NaOAc}$ ; 0.078 M  $\text{HOAc}$ ;

79 psi  $\text{CO}$ ;  $90^\circ\text{C}$

Gas Solubility at  $90^\circ\text{C}$        $\alpha_{\text{CO}} = 6.9 \times 10^{-4} \text{ M/atm}$

$\alpha_{\text{CO}_2} = 105.0 \times 10^{-4} \text{ M/atm}$

Volume of solution added ( $V_1$ ) = 90.0 mls

Total volume of reactor at  $90^\circ\text{C}$  = 120.0 mls

Density of  $\text{H}_2\text{O}$  = 0.9653 g/ml at  $90^\circ\text{C}$ ; 0.9982 g/ml at  $20^\circ\text{C}$

$V_g = 120.0 - 90.0 \times 0.9982 / 0.9653 = 26.9 \text{ mls}$

$$F = \frac{V_g}{V_1} \times \frac{1000}{RT} = \frac{26.9}{90.0} \times \frac{1000}{82.05 \times 363}$$
$$= 100.3 \times 10^{-4} \text{ M/atm}$$

$$R.F. = \frac{(F + \alpha_{CO})(F + \alpha_{CO_2})}{(\alpha_{CO_2} - \alpha_{CO})}$$
$$= \frac{(100.3 + 6.9)10^{-4} (100.3 + 105.0)10^{-4}}{(105.0 - 6.9)10^{-4}}$$
$$= 0.0224 \text{ M/atm}$$

Values for  $(f(\Delta P_T))^{-1}$  and calculated time computed from the above data at 1-psi intervals up to about 50% reaction using the "best value" rate constants\* for equation 19 from Table X, are given in Table F-I. Also included are the time values taken from the experimental records for experiments 207 and 230.

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\*  $k_1' = 2.7 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$ ;  $k_2' = 2.1 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ ;  
 $k_3' = 6.2 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$

TABLE F-I

COMPARISON OF EXPERIMENTAL AND CALCULATED PRESSURE RECORDS

(Figure 25, Section III-10)

$\Delta P_T^*$	$(f(\Delta P_T))^{-1}$ min psi <sup>-1</sup>	Time (min)		
		Calculated	Experimental	
			No 207	No 230
0	0.67	0	0	0
1	0.75	0.7	1.0	0.9
2	0.85	1.5	1.8	1.9
3	0.95	2.4	2.8	2.7
4	1.07	3.4	3.7	3.8
5	1.21	4.6	--	--
6	1.37	5.9	5.6	6.0
7	1.55	7.3	--	--
8	1.76	9.0	8.7	10.3
9	2.00	10.9	--	--
10	2.28	13.0	12.0	13.7
11	2.60	15.4	13.8	--
12	2.97	18.2		19.0
13	3.41	21.4		--
14	3.92	25.1		27.0
15	4.53	29.3		30.0
16	5.26	34.2		34.5
17	6.12	39.9		37.2
18	7.16	46.5		43.7
19	8.43	54.3		50.2
20	9.98	63.5		57.8

\* A total pressure decrease of 20 psi is equivalent to about 50% reaction.

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VII NOMENCLATURE USED IN RATE EXPRESSIONS

Rate Functions

$R = -d[CO]/dt =$  rate of CO consumption (M sec<sup>-1</sup>)

$R' = R/P_{CO} =$  rate of CO consumption at unit pressure (M atm<sup>-1</sup> sec<sup>-1</sup>)

$I =$  acid-independent rate (M sec<sup>-1</sup>)

$I' =$  acid-independent rate at unit pressure (M atm<sup>-1</sup> sec<sup>-1</sup>)

$D =$  acid-dependent rate (M sec<sup>-1</sup>)

$D' =$  acid-dependent rate at unit pressure (M atm<sup>-1</sup> sec<sup>-1</sup>)

$S =$  acid-proportionality constant for acid-dependent rate (M<sup>2</sup> sec<sup>-1</sup>)

$S' =$  acid-proportionality constant at unit pressure (M<sup>2</sup> atm<sup>-1</sup> sec<sup>-1</sup>)

$R_0 =$  acetate-independent rate (M sec<sup>-1</sup>)

$R_0' =$  acetate-independent rate at unit pressure (M atm<sup>-1</sup> sec<sup>-1</sup>)

Rate Constants

$k_1, k_2, k_3 =$  experimental rate constants in terms of [CO]

$k_1', k_2', k_3' =$  experimental rate constants in terms of  $P_{CO}$

$k_2'', k_2''' =$  rate constants for reaction in unbuffered solution (Section III-9)

$k_3'', k_4'' =$  rate constants for acid-dependent reaction (equations 15 and 16)

$k_a, k_b, k_c, k_d, k_e, k_f, k_g =$  rate constants for proposed mechanism (reaction V)

$C_n(n=1,2,3,4) = [OAc^-]$ -power series coefficients in eqn 38 for acid-dependent react.

Equilibrium Constants

$K_i =$  ionization constant of acetic acid (M)

$K_a =$  association constant for average silver-acetate complex ( $\overline{AgOAc}$ ) from  $Ag^+$  and  $OAc^-$  (M<sup>-1</sup>)

$K_1, K_2 =$  association constants for  $AgOAc$  and  $Ag(OAc)_2^-$  from  $Ag^+$  and  $OAc^-$  (eqn 37)

$K_c =$  formation constant, incorporating  $[H_2O]$ , for intermediate complex from  $Ag^+$ , CO and  $H_2O$  in proposed mechanism (reaction V(d))

$K_c' =$  formation constant, incorporating  $[H_2O]$ , for intermediate complex from  $AgOAc$ , CO and  $H_2O$  in proposed mechanism (reaction V(h))

$\alpha_{CO} =$  CO solubility coefficient (M/atm)

$\alpha_{CO_2} =$  CO<sub>2</sub> solubility coefficient (M/atm)