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ANODIC DISSOLUTION OF SILVER IN
AQUEOUS SOLUTIONS

BY

JAGDISH SHANTILAL SANGHVI

A

THESIS

submitted to the faculty of the
UNIVERSITY OF MISSOURI AT ROLLA
in partial fulfillment of the requirements for the
Degree of
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
Rolla, Missouri

1965

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I. INTRODUCTION

Silver and platinum, although not used extensively in industry, find considerable use in specialized work. Silver, because of its much lower cost, is used to a greater extent than platinum. Since silver has a high position in the electromotive series, it is very resistant to chemical attack. It is unaffected by alkaline conditions even at high temperatures and hence silver is used in ladles and molds for producing pure sodium and potassium hydroxides. This and its excellent electrical conductivity makes it a very useful material in circuitry.

It has been reported in the literature (12, 13) that when active metals such as magnesium, zinc, and cadmium dissolve anodically in aqueous solutions, a greater amount of metal is found in solution than indicated by Faraday's law. This deviation from Faraday's law has been explained as due to the chunk effect (disintegration) (15), or to valencies less than that of the normal ion (13).

The present investigation was carried out with the intention of determining if a similar deviation occurs for the anodic dissolution of a noble metal such as silver. The existence of such a phenomenon with silver would necessarily be explained by a disintegration of the electrode rather than uncommon valence ion formation.

II. LITERATURE REVIEW

This review of literature is divided into two parts:

- (1) anodic dissolution of silver in aqueous solutions, and
- (2) the study of the relationship between the current density and potential of the silver anode in aqueous solutions.

Anodic Dissolution of Silver in Aqueous Solutions.

The literature reveals that work has been done on the behavior of silver undergoing anodic dissolution in aqueous solutions. No information is available for the deviation from Faraday's law of silver undergoing such dissolution.

Burton (1) prepared colloidal solutions of gold, silver, bismuth, and lead in pure water using potentials of 30 to 60 volts and currents of 6.5 to 7.5 amperes. He observed clouds of finely divided metal that scattered from these metal cathodes during the sparking which remained suspended in the water for a time depending on the nature of the electrode metal. The mechanism of the process was explained as involving vaporization of the metal at the electrode with its dispersion and condensation in the solution.

When active metals such as zinc or cadmium are dissolved anodically in neutral salt solutions containing nitrate, chlorate, or perchlorate ions, the number of coulombs required to dissolve one gram equivalent of the metal is

frequently less than one Faraday. This deviation from Faraday's law has been explained by disintegration of the metal (12), complex ion formation (2), and by uncommon valence ion formation. (13)

James and Stoner (12) studied the anodic dissolution of zinc in a three per cent potassium nitrate solution at current density of $0.060 \text{ amp}\cdot\text{cm}^{-2}$. They observed the formation of a dark-colored film on the surface of the zinc anode and found an apparent valence less than two.

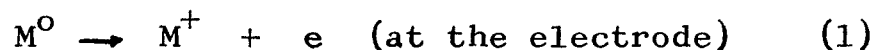
Craig, et al., found the silver particles (sediment) at the bottom of the anode beaker during the anodic dissolution of silver in silver-perchloric acid coulometer (16). The percentage of sediment found in the anode beaker varied from 0.015 to 16.2 depending on the preparation of the silver anodes. But, they did not give any explanation for the sediment found in the anode beaker.

Vermilyea (14) also found that when silver is dissolved electrolytically in a one normal silver nitrate solution (pH = 3) at about $1.0 \text{ amp}\cdot\text{cm}^{-2}$, the surface of the silver electrode usually becomes covered with a dark-colored material known as "anode slime". This substance either continuously or periodically falls from the surface of the electrode downward through the solution. This anode slime was analyzed and found to be substantially all silver. He proposed a mechanism for the formation of these metallic particles associated with the electrodeposition of silver from salt

solutions. It is believed that during the deposition that most of the surface of the electrode remains inactive. This is because of impurities present in the solution which adsorb on the electrode surface and cause passivation. In the dissolution process, a similar passivation would occur and dissolution would take place only on discrete areas. Thus, some of the sections of the metal surface would remain passive and inhibit dissolution, causing the formation of the silver particles which constitute the anode slime.

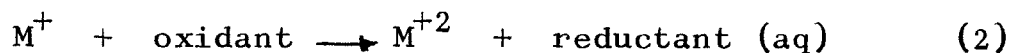
Del Boca (2) studied the dissolution of various metals in liquid ammonia. To account for deviations from Faraday's law, he proposed that the dissolving metal entered into the solution by the formation of complex ions such as $Zn \cdot Zn^{+2}$, $Cd \cdot Cd^{+2}$, or $Al_2 \cdot Al^{+3}$.

Davidson and co-workers (13) give considerable support to the "uncommon valence ion" concept. This was first proposed by Epelboin (3) to explain the deviation from Faraday's law of zinc and cadmium undergoing anodic dissolution. The hypothesis is that the dissolution of the metal is a stepwise oxidation, the first step being the oxidation of the metal to the unipositive ion at the anode:

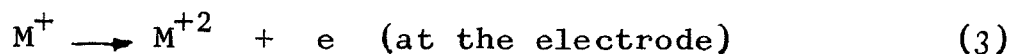


The unipositive ion would be expected to be very unstable,

readily forming the normal bipoisitive ion as the second step. There are two ways in which this second step could occur. First, by chemical oxidation by an oxidizing agent in the solution, that is,



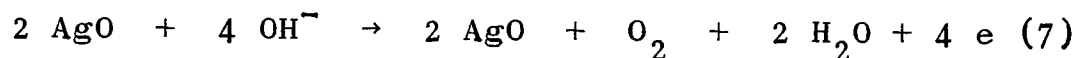
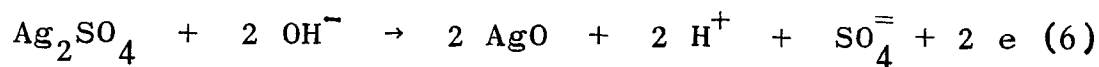
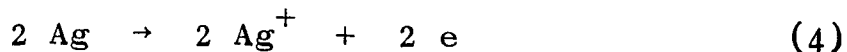
The alternate way the second step could occur is by further oxidation of the unipoisitive ion to the bipoisitive ion at the surface of the electrode, that is,



With non-reducible electrolytes, reaction (2) cannot occur and consequently a valence of two would be observed according to reactions (1) and (3). With reducible electrolytes, the two possible mechanisms for the second step would be competitive with the predominant one depending on the nature of the oxidizing electrolyte and the conditions of the experiment. Thus, valencies between 1 and 2 should be observed.

The Relationship between the Current Density and the Potential of the Silver Anode in Aqueous Solutions.

Jones and Thirsk (7) investigated the process occurring at silver anodes in 2 N sulfuric acid at a current density of $0.040 \text{ amp}\cdot\text{cm}^{-2}$. They concluded that the stepwise reaction occurs as follows:



In the oxidized state, the electrode seems to function as an oxide electrode and oxygen evolution occurs at the surface.

Bockris and Mehl (10) found that for the deposition and dissolution processes for Ag from AgClO_4 , the slopes of the anodic and cathodic Tafel-lines are the same. Silver electrodes were prepared by "thermal etching" (heating a thin wire in an atmosphere of hydrogen). They observed that surface diffusion of adions is the principal rate determining step at low overpotentials. At high overpotentials, the transfer of ions from the solution to the electrode is the principal rate determining step down to concentrations of 10^{-4} to 10^{-5} moles/liter. At lower concentrations than these, the ionic transfer rate seems to be controlling at all current densities. They, and also Gerischer (4), found that the exchange current for the system Ag/Ag^+ is independent of the concentration of silver ions in solutions below 10^{-4} to 10^{-5} moles/liter.

Mathur, Karuppanan, and Anantharaman (9) studied the relationship between current density and potential of silver and copper undergoing dissolution in different stripping agents at 25°C under unstirred conditions. The potential:

of the silver anode in 1.67 N sodium nitrate was found to be more noble than in 1.67 N nitric acid. They obtained a relationship between the current and potential of the silver anode at current densities greater than 0.10 amp.cm^{-2} . The slope of the linear portion of the curve for 1.67 N sodium nitrate was 0.231 ohms and in 1.67 N nitric acid was 0.270 ohms. They concluded that the solutions exhibiting large values of slope will evolve oxygen on a rough surface even at apparently low current densities due to the non-uniform distribution of current over the surface.

L. Redey (11) conducted an investigation of the silver anode in 1.0 N silver nitrate, 1.0 N potassium nitrate, and 1.0 N potassium chloride solutions. In 1.0 N potassium nitrate, the potential of the silver anode at zero current density was indefinite. As current was applied, the potential became fairly definite, however, it was not as reproducible as in 1.0 N silver nitrate. The variation of polarization was greater in potassium nitrate than in silver nitrate. This is easily understood in terms of a more stable silver ion concentration in silver nitrate solution. In potassium nitrate solution, the silver ions which are formed under the influence of current in the limiting (double) layer between the electrode and electrolyte determine the reversible potential and the variation of current causes the concentration of silver ions in the layer to change. Such a

variation must be considered to exist and the concentration of silver ions will fall off almost to zero at very small currents. They also determined that stirring had a more significant effect in the potassium nitrate than in silver nitrate. In stirred solutions, the potential of the silver anode became less noble. The silver anode in 1.0 N potassium chloride solution acted as a Ag/AgCl electrode which is considered to be an electrode of second type. This type of electrode should be only slightly polarizable but it was found to be polarized at even low current densities.

In 1.0 N potassium hydroxide solution, oxygen overvoltage measurements have been made for the silver anode (8). Linear Tafel-lines were obtained but reproducibility of the slope was poor. Values of $\alpha = 0.34 \pm 0.01$ were obtained. The smaller values of α were possibly due to inclusion of a resistance overvoltage arising from surface films on the electrode. They mentioned that the resistance probably was not from the AgO layer, since this material has been found to be a good electrical conductor. They observed that a further oxidation of AgO to Ag₂O₃ occurs to some extent. The resistive properties of the latter material are unknown.

Hickling and Taylor (5) studied the anodic behavior of silver in 1.0 N sodium hydroxide. They found that the anodic polarization of silver remained the same as the alkalinity of the electrolyte was decreased, but that the

formation of silver monoxide increased. In an electrolyte of pH less than 9, the silver anode did not become passive and the process was merely the dissolution at the anode.

III. EXPERIMENTAL

The purpose of this investigation was to study the anodic dissolution of silver in salt solutions and to determine the effect of varying amounts of silver ions present in the solution. The solutions included potassium sulfate, potassium nitrate, and ammonium nitrate.

The experimental plan consisted of the following major phases: (1) the effect of various electrolytes (potassium sulfate, potassium nitrate, and ammonium nitrate) and current density on the apparent valence of silver undergoing anodic dissolution, and (2) the effect of concentration of silver ions and current density on the dissolution potential of silver. Studies were made at temperatures of 25°C and 50°C.

Materials

The list of the materials used in this investigation are given in the appendix, page 81.

1. The Apparent Valence of Silver Undergoing Anodic Dissolution in Various Electrolytes at 25°C and 50°C.

Apparatus. The apparatus consisted of an electrolytic cell with separated compartments of 300 milliliter

capacity, a silver anode, a platinized-platinum cathode, a sensitive milliammeter, a power source, a decade type resistance box, and a knife switch. A diagram of the apparatus is shown in Figure 1, page 12. A timer with one-second divisions was used for measuring the elapsed time. A 400 milliliter beaker was used to collect the anolyte and a Gooch crucible was used to collect the precipitate of silver chloride for the determination of silver content by a gravimetric method. The cell was immersed in a water bath controlled to within $\pm 0.1^{\circ}\text{C}$.

Procedure. A specimen of known cross-sectional area was prepared under vacuum by melting silver of 99.999 percent purity in a graphite mold. The diameter of the silver specimen was determined with a micrometer. The sample was then mounted in lucite with a metallographic press or in teflon by press fitting. The electrode was prepared as previously described (6). It was polished immediately before each run according to the procedure listed in the appendix, page 82. Approximately 200 milliliters of electrolyte were transferred into the electrolytic cell. The cell was then placed in the constant temperature bath so as to ensure complete submergence of the solution. About one-half hour was allowed to bring the system to constant temperature before starting a run. After that, the mounted metal anode and the platinized-platinum cathode were put into the anodic and cathodic

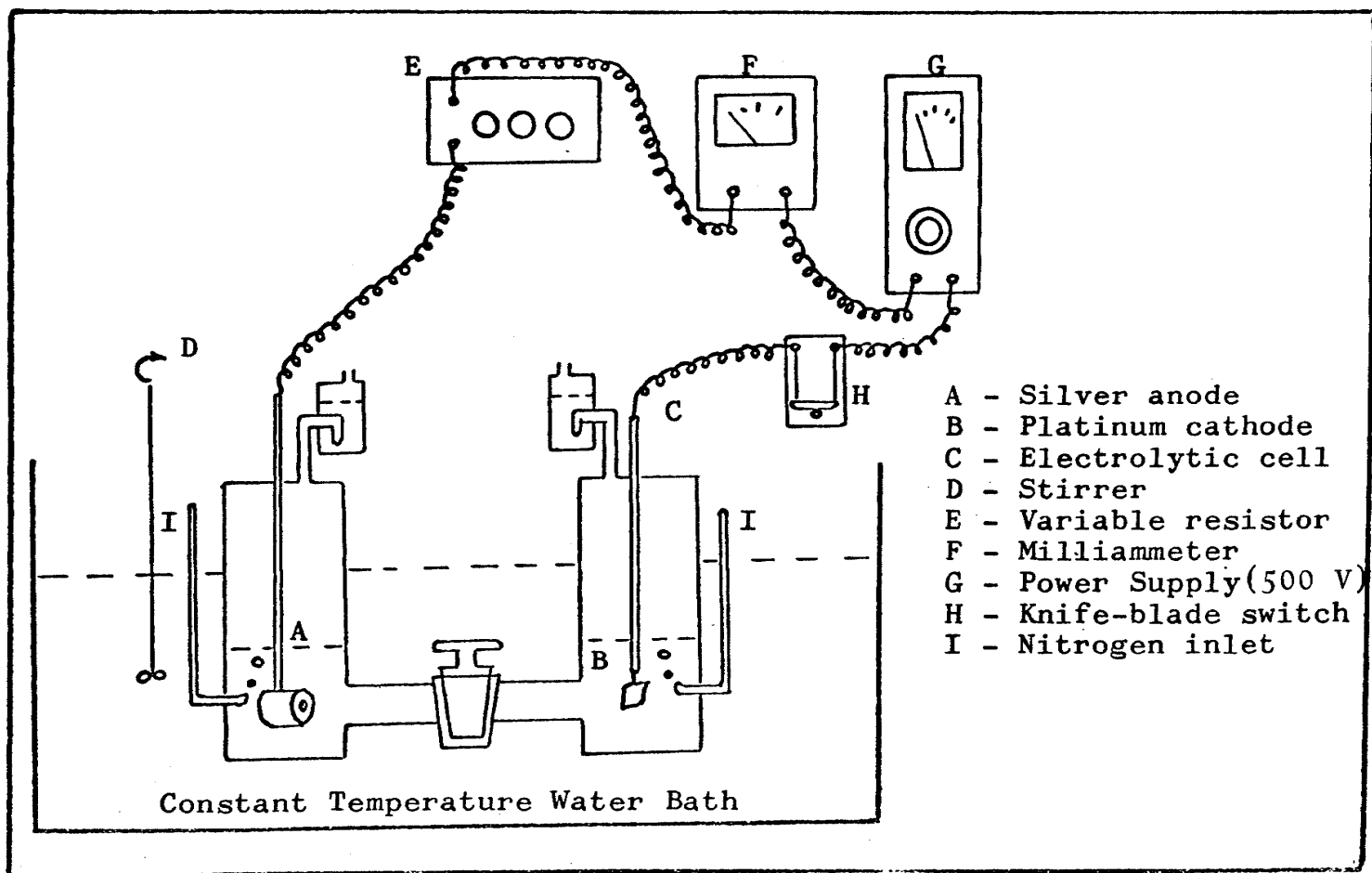


Figure 1. Diagram of apparatus used for measurement of apparent valence of silver undergoing anodic dissolution.

compartments respectively, and were connected into the external circuit (see Figure 1, page 12). Nitrogen gas was bubbled through the anodic compartment. To begin a run, the knife-blade switch was closed and the current was kept at a steady rate by means of the variable resistance. The timer and milliammeter were used for measuring the number of coulombs passed. At the end of a test run, the anolyte was collected in a beaker. If any film was formed on the surface of the electrode, it was transferred from the surface into the beaker. The film was dissolved by adding 10 to 15 milliliters of concentrated nitric acid to the anolyte, then neutralizing it with concentrated ammonium hydroxide. The resultant solution was made acidic by adding 1 : 1 nitric acid. The silver ions were precipitated as silver chloride with an addition of excess sodium chloride solution. The solution was heated to boiling, stirred for a couple of minutes to coagulate the precipitate, and was allowed to cool to room temperature. A test for complete precipitation was made by adding additional sodium chloride solution. The precipitate of silver chloride was collected carefully in a Gooch crucible of known weight. The crucible was heated in an oven to constant weight. The weight of silver chloride thus determined was used to calculate the weight loss of the silver from the anode. The same procedure was employed for all electrolysis experiments.

Data and Results. The anodic dissolution of silver was observed in three electrolytes, one normal solutions of potassium sulfate, potassium nitrate, and ammonium nitrate. A brief summary of the results for each follows.

Potassium Sulfate. The anodic dissolution of silver in 1.00 N potassium sulfate was carried out at a temperature of 25°C and at current densities of 0.00147 and 0.00737 amp. cm⁻². Data from these runs are shown in Table I, page 15. It can be seen that the apparent valence increases with current density. At current densities greater than 0.00737 amp. cm⁻², bubbles of gas were observed forming on the surface of the electrode, thus accounting for the increased valence. The gas evolved was most probably oxygen.

Potassium Nitrate. Silver was anodically dissolved in 1.00 N potassium nitrate at current densities varying from 0.00147 to 0.1265 amp. cm⁻² at temperatures of 25°C and 50°C. The data collected are shown in Tables II and III, pages 16 and 17. It can be seen that the apparent valence is close to the normal value at all current densities at temperatures of 25°C and 50°C. At a current density of 0.1265 amp. cm⁻², a black colored film was observed on the surface of the electrode at 25°C. At a temperature of 50°C, a black colored film was observed at all current densities.

TABLE I

The Apparent Valence of Silver in 1.00 N K_2SO_4 at 25°C

Time (sec)	Current Density* (amp.cm ⁻²)	Weight of Silver		Apparent Valence
		Calc. (gm)	Expt. (gm)	
36,000	0.00147	0.0402	0.0396	1.02
1,800	0.00737	0.0402	0.0336	1.19

* Area of the electrode = 0.678 cm²

TABLE II

The Apparent Valence of Silver in 1.00 N KNO_3 at 25°C

Time (sec)	Current Density* (amp·cm ⁻²)	Weight of Silver		Apparent Valence
		Calc. (gm)	Expt. (gm)	
36,000	0.00147	0.0535	0.0547	0.98
7,200	0.00737	0.0535	0.0543	0.98
3,600	0.01475	0.0535	0.0539	0.99
1,800	0.02950	0.0535	0.0550	0.97
1,800	0.04425	0.0802	0.0837	0.96
1,800	0.04425	0.0802	0.0828	0.97
1,440	0.05899	0.0855	0.0855	1.00
1,800	0.05899	0.1069	0.1106	0.97
1,800	0.05899	0.1069	0.1095	0.98
1,800	0.05899	0.1069	0.1079	0.99
900	0.07375	0.0668	0.0689	0.97
1,800	0.07375	0.1337	0.1362	0.98
1,800	0.1032	0.1872	0.1914	0.98
1,800	0.1032	0.1872	0.1908	0.98
1,800	0.1264	0.2406	0.2442	0.98
1,800	0.1264	0.2406	0.2448	0.98

* Area of the electrode = 0.678 cm^2

TABLE III

The Apparent Valence of Silver in 1.00 N KNO_3 at 50°C

Time (sec)	Current Density* (amp·cm ⁻²)	Weight of Silver		Apparent Valence
		Calc. (gm)	Expt. (gm)	
36,000	0.0020**	0.0595	0.0593	1.00
9,000	0.0400	0.1135	0.1093	1.04
3,600	0.1000	0.1135	0.1198	0.95

* Area of the electrode = 0.282 cm²
 ** Area of the electrode = 0.739 cm²

Ammonium Nitrate. There was no effect of current density on the apparent valence of silver undergoing anodic dissolution in 1.00 N ammonium nitrate at temperatures of 25°C and 50°C. The current density was varied from 0.00140 to 0.1265 amp. cm⁻². At a temperature of 25°C, only at high current density was a black film observed on the surface, but at 50°C, a black film formed on the surface at all current densities. The data are shown in Tables IV and V, pages 20 and 21.

Sample Calculations. The methods used to calculate the apparent valence in potassium sulfate, potassium nitrate, and ammonium nitrate solutions were the same. The data from experiments in 1.00 N potassium sulfate solution (Table I, page 15) have been used to illustrate the calculations involved in this part of the experimentation.

Calculation of the Apparent Weight of Silver Dissolved from Coulombic Data. The apparent weight of silver dissolved according to Faraday's law assuming a normal valence of one was calculated as follows:

$$W_a = \frac{I t A}{n F} \quad (8)$$

where,

W_a = apparent weight of silver in gms

t = time interval of run (= 36,000 secs)

I = current (= 0.0010 amp)

A = atomic weight of silver (= 107.88)

F = Faraday constant (= 96,500 amp·sec/equivalent)

n = normal cationic charge of silver (= 1).

Therefore,

$$W_a = \frac{(0.0010)(36,000)(107.88)}{(96,500)(1)}$$

$$= 0.0402 \text{ gm.}$$

Calculation of the Apparent Valence. The apparent valence was calculated by the equation:

$$V_i = \frac{W_a V_n}{W_e} \quad (9)$$

where,

V_i = apparent valence

V_n = normal valence

W_a = weight of silver apparent = weight of silver determined from coulombic data, gm

W_e = weight of silver experimental = weight of silver determined by precipitation of silver ions as silver chloride, gm.

Therefore,

$$V_i = \frac{(0.0402)(1)}{(0.0396)} = 1.02 .$$

TABLE IV

The Apparent Valence of Silver in 1.00 N NH_4NO_3 at 25°C

Time (sec)	Current Density* (amp·cm ⁻²)	Weight of Silver		Apparent Valence
		Calc. (gm)	Expt. (gm)	
39,600	0.001408	0.0577	0.0588	0.97
1,800	0.05622	0.1069	0.1079	0.99
1,800	0.05622	0.1069	0.1083	0.99
1,800	0.12649	0.2406	0.2446	0.98
1,800	0.12649	0.2406	0.2443	0.99

* Area of the electrode = 0.712 cm²

TABLE V

The Apparent Valence of Silver in 1.00 N NH_4NO_3 at 50°C

Time (sec)	Current Density* (amp·cm ⁻²)	Weight of Silver		Apparent Valence
		Calc. (gm)	Expt. (gm)	
36,000	0.0020**	0.0595	0.0593	1.00
9,000	0.0400	0.1135	0.1165	0.97
3,600	0.1000	0.1135	0.1165	0.97

*Area of the electrode = 0.282 cm²

**Area of the electrode = 0.739 cm²

2. Dissolution Potential of Silver Undergoing Anodic Dissolution in Various Electrolytes at 25°C and 50°C.

Apparatus. The apparatus consisted of an electrolytic cell with separated compartments of 300 milliliter capacity, a silver anode, a platinized-platinum cathode, a reference electrode (one normal calomel), a milliammeter, a decade type resistance box, a power supply, and an electrometer. A diagram of the apparatus is shown in Figure 2, page 23.

Procedure. A specimen of known cross-sectional area was prepared under vacuum by melting silver of 99.999 percent purity in a graphite mold. The silver specimen was machined to an accurate diameter in a lathe and then pressed into a teflon mounting. The electrode was prepared as previously described (6). The electrode was polished immediately before each run according to the procedure listed in the appendix, page 82, and it was etched in dilute nitric acid. Approximately 200 milliliters of electrolyte were transferred into the cell, the cell was placed in the constant temperature bath so as to ensure complete submergence of the solution. About one-half hour was allowed to bring the system to constant temperature before starting a run. The silver anode and the platinized-platinum cathode were immersed into the anodic and cathodic compartments

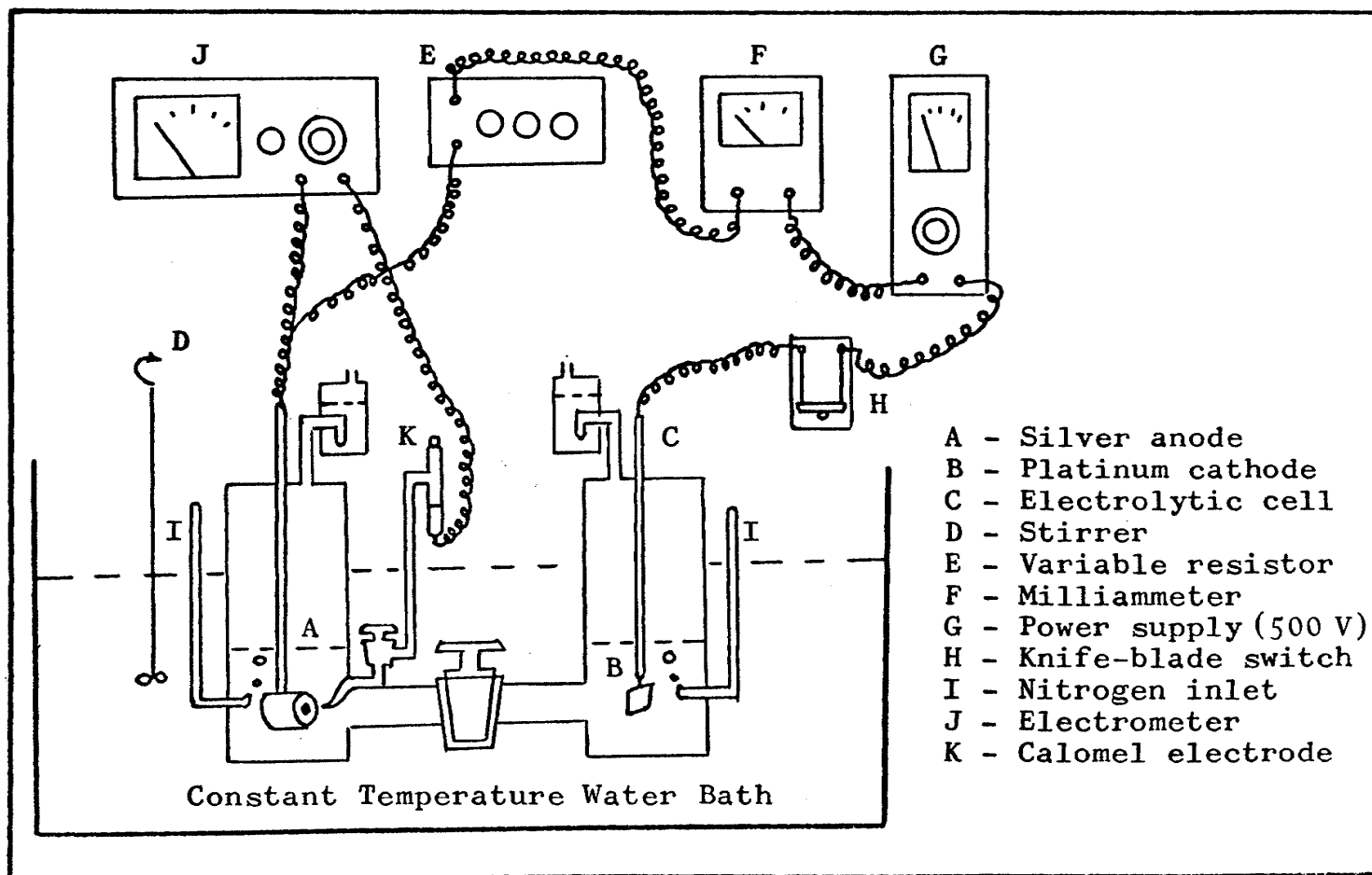


Figure 2. Diagram of apparatus used for measurement of dissolution potential of silver at various current densities.

respectively, and were connected to the external circuit. The silver anode and the calomel electrode were connected to the electrometer. Nitrogen gas was bubbled through the anodic compartment during the run. In the absence of applied current, the potential of the silver electrode was measured at intervals of 15 minutes until it reached a constant value. Similar measurements were then made at different current densities.

Data and Results. Dissolution potentials of silver were obtained in different electrolytes of potassium nitrate and ammonium nitrate with varying silver nitrate concentration. The ionic strength was held constant at 1.00 gram-equivalent per liter. All of the solutions were prepared with triply distilled water. The time behavior of the potential is listed in the appendix, page 83. A brief summary of the results for each follows.

Electrolyte: 1.00 N Potassium Nitrate.

Dissolution potentials were obtained at current densities ranging from zero to $0.080 \text{ amp}\cdot\text{cm}^{-2}$ at temperatures of 25°C and 50°C . The data are shown in Tables VI and VII, pages 25 and 26, respectively. A plot of overpotential as a function of current density is shown in Figures 3 and 4, pages 27 and 28, respectively. The overpotential is the difference between the steady potential at a constant current density and

TABLE VI
 Dissolution Potential of the Silver Electrode in
 1.00 N KNO₃ at 25°C

I x 10 ³ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b		Overpotential (volts)	
	Run 1	Run 2 ^c	Run 1	Run 2
0.00	0.463	0.447	0.018	0.002
0.20	0.601	0.610	0.156	0.165
0.40	0.660	0.626	0.215	0.181
1.00	0.672	0.651	0.227	0.206
2.00	0.690	0.671	0.245	0.226
4.00	0.700	0.691	0.255	0.246
8.00	0.721	0.716	0.276	0.271
20.00	0.761	0.726	0.316	0.281
40.00	0.792	0.761	0.347	0.316
80.00	0.880	-	0.435	-

Calculated reversible potential = 0.445 volts

^aArea of the electrode = 0.608 cm²

^bNormal hydrogen scale

^cClosed system

TABLE VII
 Dissolutions Potential of the Silver Electrode in
 1.00 N KNO₃ at 50° C

I x 10 ³ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b		Overpotential (volts)	
	Run 1	Run 2	Run 1	Run 2
0.00	0.447	0.446	0.057	0.056
0.20	0.591	0.582	0.201	0.192
0.40	0.591	0.606	0.201	0.216
1.00	0.621	0.621	0.231	0.231
2.00	0.651	0.641	0.261	0.251
4.00	0.671	0.662	0.281	0.272
8.00	0.690	0.683	0.300	0.293
20.00	0.711	0.709	0.321	0.319
40.00	0.750	0.732	0.360	0.342
80.00	0.782	0.756	0.392	0.366

Calculated reversible potential = 0.390 volts

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

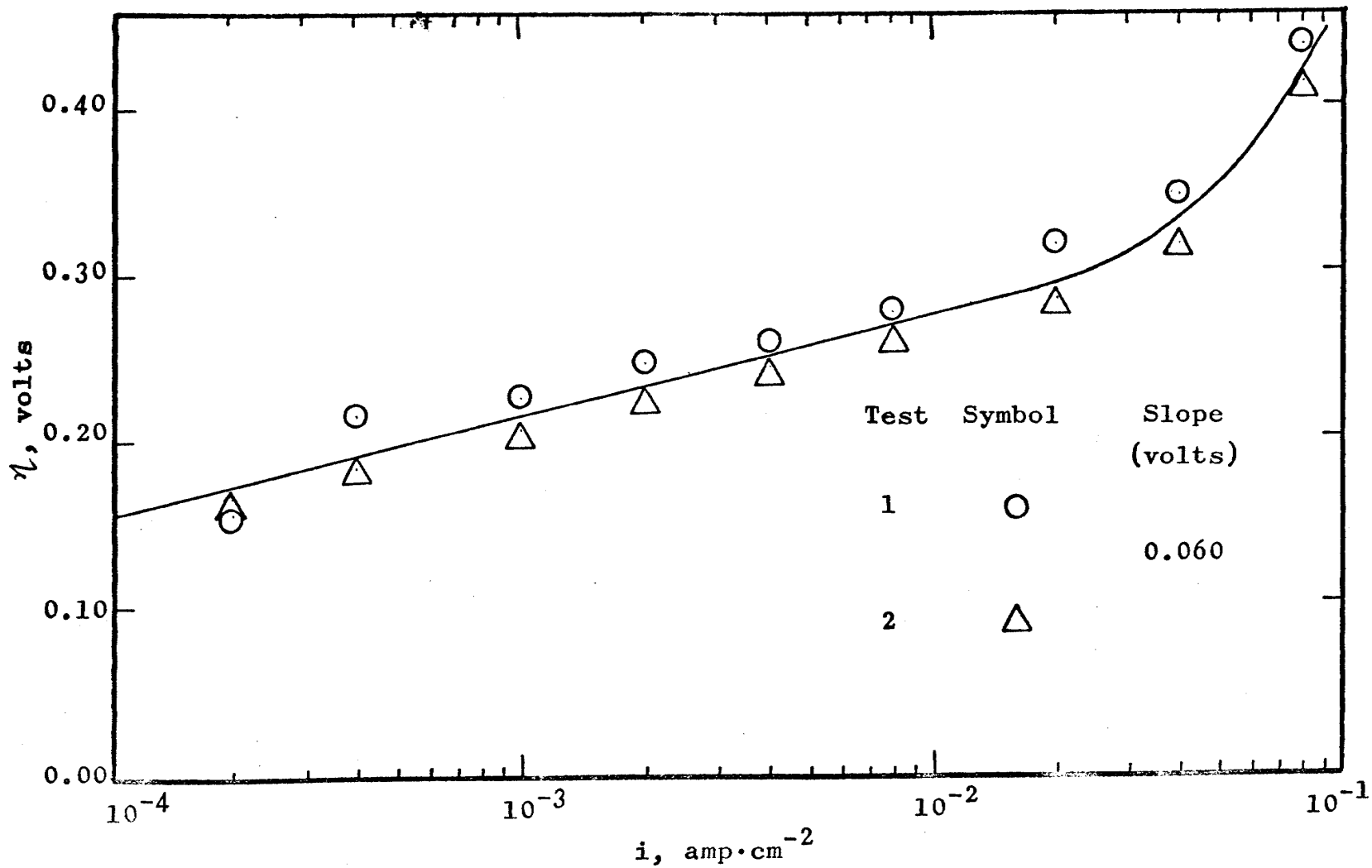


Figure 3. The Tafel curve for the anodic dissolution of silver in 1.00 N KNO₃ at 25°C.

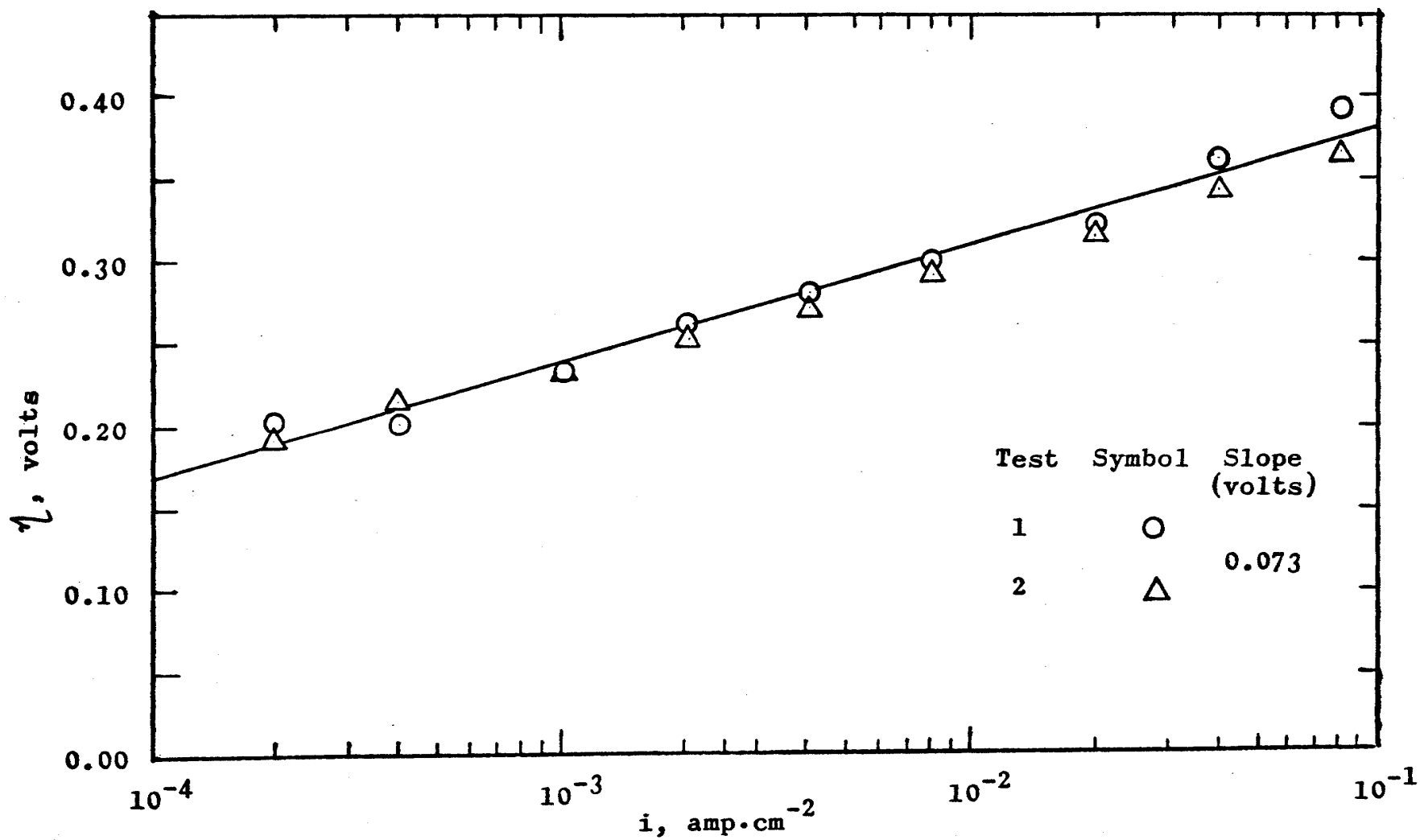


Figure 4. The Tafel curve for the anodic dissolution of silver in 1.00N KNO₃ at 50°C.

the reversible potential of the electrode at the same experimental conditions. The reversible potential of the silver electrode in electrolyte having no silver ions was calculated using the Nernst equation assuming the activity of silver ions to be 10^{-6} .

Electrolyte: 1.00 N Ammonium Nitrate. The potentials of the silver electrode undergoing anodic dissolution at temperatures of 25 and 50°C are shown in Tables VIII and IX, pages 30 and 31, respectively. In 1.00 N ammonium nitrate solution at temperatures of 25 and 50°C, the dissolution potentials were not reproducible. The current density ranged from zero to 0.090 amp·cm⁻². A plot of overpotential versus current density is shown in Figures 5 and 6, pages 32 and 33, respectively.

Electrolyte: 0.99 N Potassium Nitrate - 0.01 N Silver Nitrate. The potential of the silver electrode as a function of current density at a temperature of 25°C in the electrolyte is shown in Table X, page 34. Figure 7, page 35, shows the relationship between the overpotential and current density. The range of current density was from zero to 0.025 amp·cm⁻². A salt bridge of 1.00 N ammonium nitrate was used.

TABLE VIII

Dissolution Potential of the Silver Electrode in
1.00 N NH_4NO_3 at 25° C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b				Overpotential (volts)			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
0.00	0.369	0.396	0.461	0.476	-0.076	-0.049	0.016	0.031
0.20	0.621	0.631	0.610	0.601	0.176	0.186	0.165	0.156
0.40	0.641	0.652	0.631	0.623	0.196	0.207	0.186	0.178
1.00	0.661	0.671	0.651	0.646	0.216	0.226	0.206	0.201
2.00	0.681	0.686	0.671	0.666	0.236	0.241	0.226	0.221
4.00	0.700	0.703	0.686	0.691	0.255	0.258	0.241	0.246
8.00	0.720	0.721	0.711	0.711	0.275	0.276	0.266	0.266
20.00	0.749	0.741	0.742	0.731	0.304	0.296	0.297	0.286
40.00	0.772	0.762	0.776	0.751	0.327	0.317	0.331	0.306
80.00	0.802	0.811	0.831	0.791	0.357	0.366	0.386	0.346

Calculated reversible potential = 0.445 volts

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE IX

Dissolution Potential of the Silver Electrode in
1.00 N NH_4NO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential ^b (volts)		Overpotential (volts)	
	Run 1	Run 2	Run 1	Run 2
0.00	0.433	0.337	0.043	-0.053
0.20	0.576	0.576	0.186	0.186
0.40	0.596	0.600	0.206	0.210
1.00	0.621	0.626	0.231	0.236
2.00	0.641	0.646	0.251	0.256
4.00	0.666	0.666	0.276	0.276
8.00	0.681	0.686	0.291	0.296
20.00	0.711	0.711	0.321	0.321
40.00	0.741	0.741	0.351	0.351
80.00	0.781	0.781	0.391	0.391

Calculated reversible potential = 0.390 volts

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

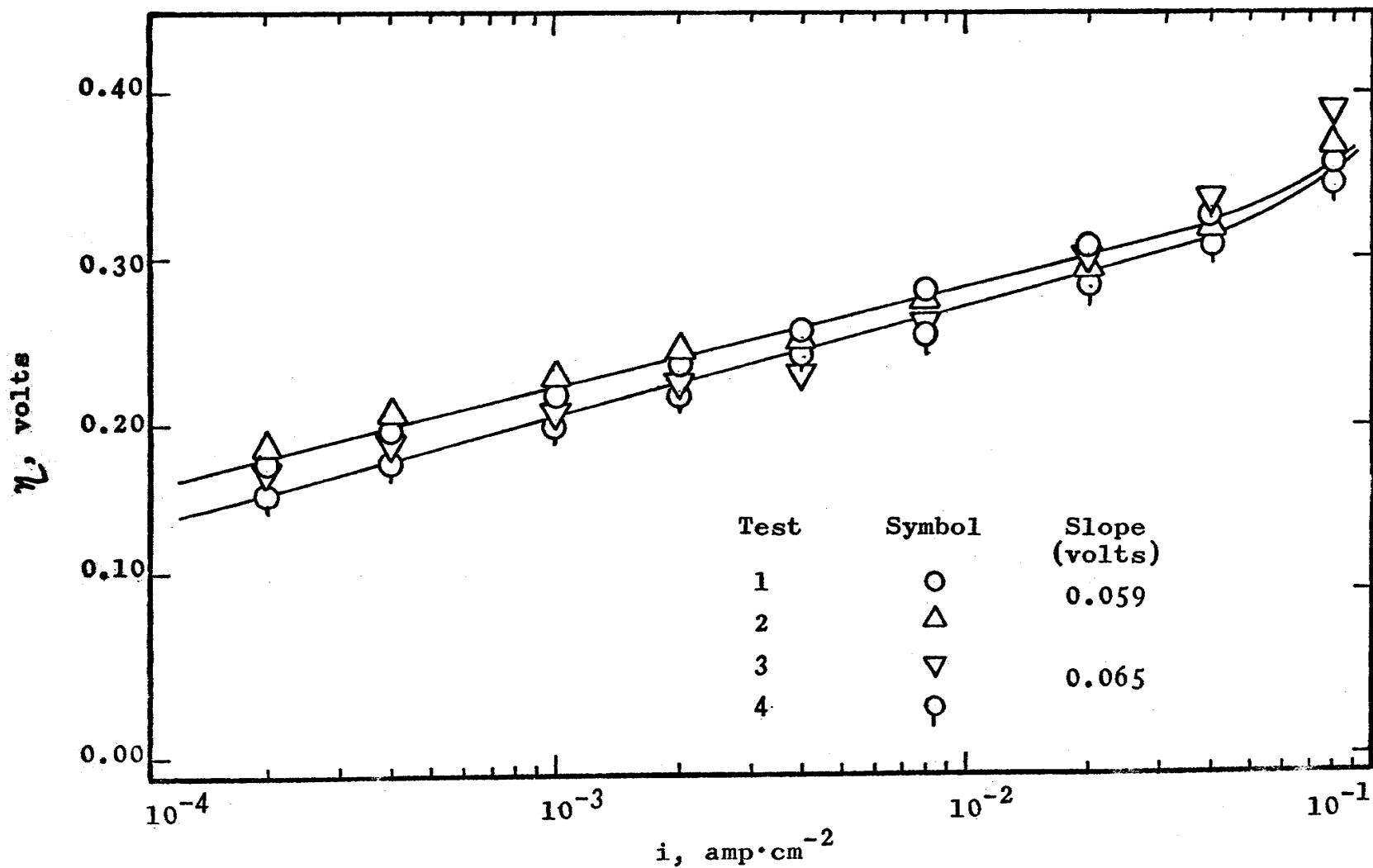


Figure 5. The Tafel curves for the anodic dissolution of silver in 1.00 N NH_4NO_3 at 25°C.

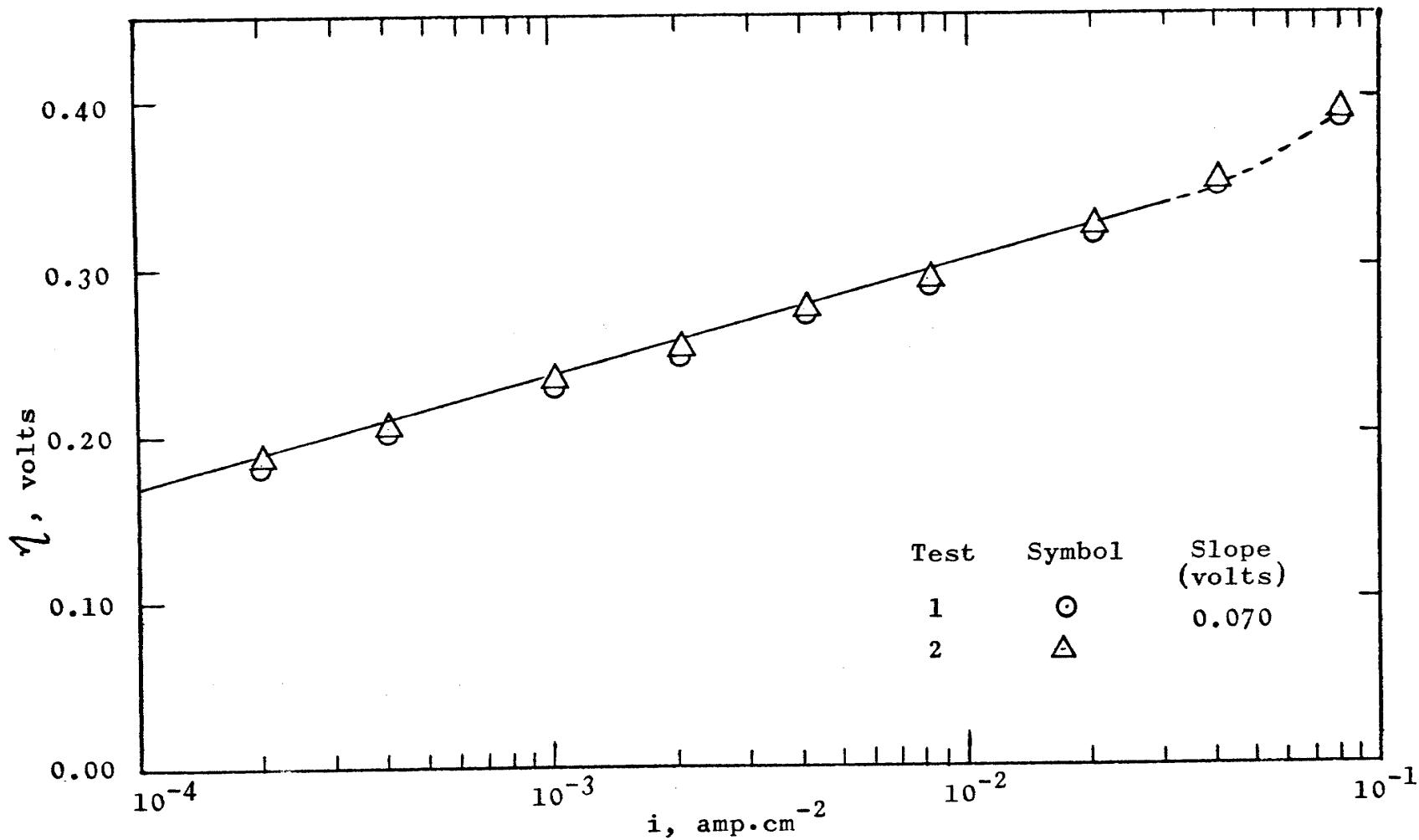


Figure 6. The Tafel curve for the anodic dissolution of silver in 1.00N NH_4NO_3 at 50°C .

TABLE X

Dissolution Potential of the Silver Electrode in
 0.99 N KNO_3 - 0.01 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential (volts)			Overpotential (volts) ^b		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
0.00	0.676	0.656	0.661	0.025	0.005	0.010
0.16	0.686	0.670	0.669	0.035	0.019	0.018
0.25	0.690	0.672	0.672	0.039	0.021	0.021
0.42	0.692	0.679	0.679	0.041	0.028	0.028
0.70	0.699	0.681	0.682	0.048	0.030	0.031
1.10	0.702	0.689	0.689	0.051	0.038	0.038
1.60	0.710	0.692	0.692	0.059	0.041	0.041
2.80	0.721	0.702	0.702	0.070	0.051	0.051
4.00	0.731	0.711	0.711	0.080	0.060	0.060
6.00	0.740	-	-	0.089	-	-
8.00	0.749	0.729	0.723	0.098	0.078	0.072
15.00	0.762	0.741	0.741	0.111	0.090	0.090

Calculated reversible potential = 0.651 volts

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

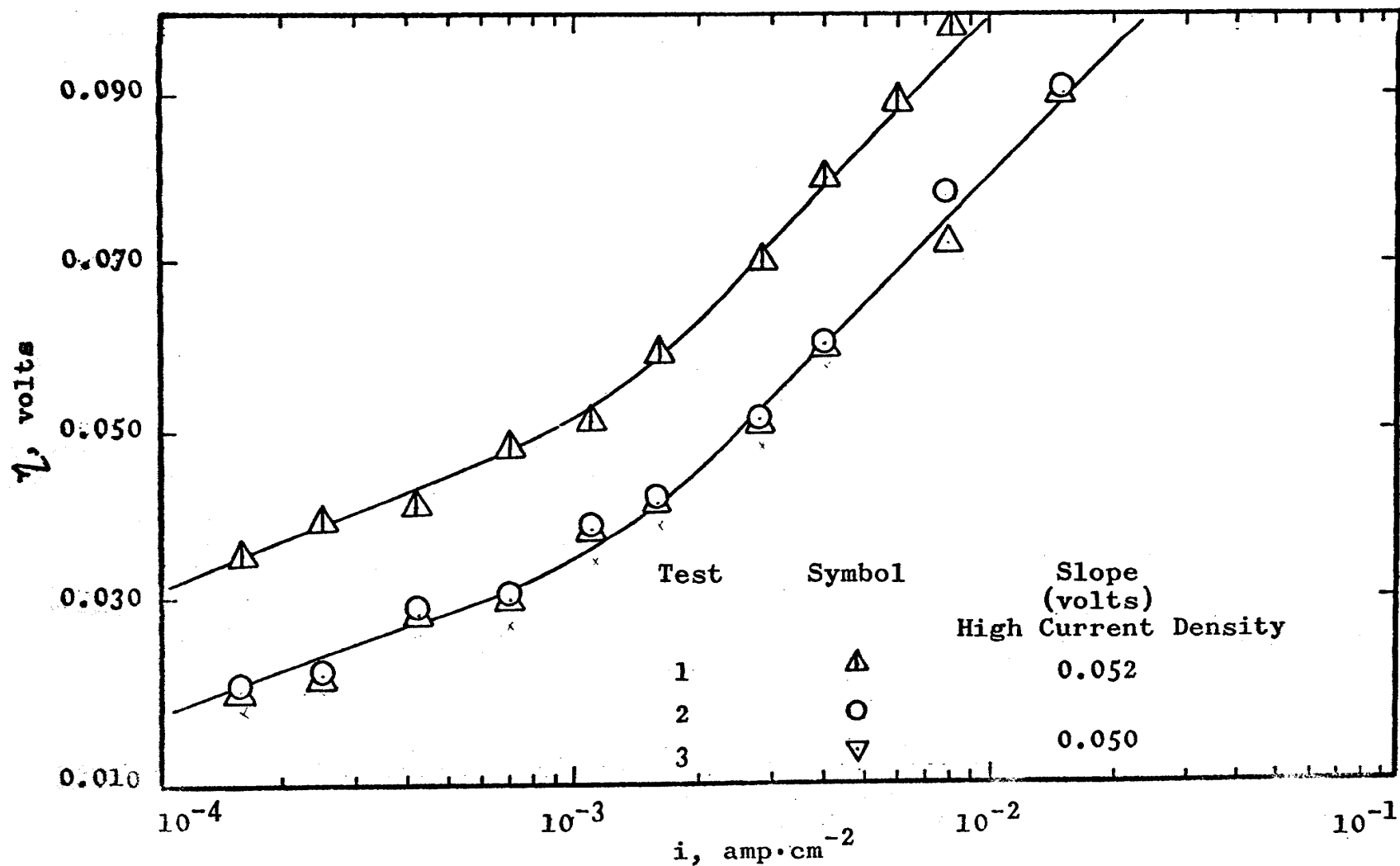


Figure 7. The Tafel curves for the anodic dissolution of silver in 0.99 N KNO_3 - 0.01 N AgNO_3 at 25°C.

Electrolyte: 0.97 N Potassium Nitrate - 0.03 N Silver Nitrate. The potential of the silver electrode at 25°C was measured at various current densities. The data are shown in Table XI, page 37. In Figure 8, page 38, the overpotential is plotted as a function of current density. The current density was varied from zero to 0.060 amp·cm⁻². 1.00 N ammonium nitrate solution was used in the salt bridge.

Electrolyte: 0.90 N Potassium Nitrate - 0.10 N Silver Nitrate. At a temperature of 25°C, potentials of the silver electrode undergoing anodic dissolution at various current densities were obtained and are recorded in Table XII, page 39. The current density was varied from zero to 0.025 amp·cm⁻². 1.00 N ammonium nitrate solution was used in the salt bridge. Overpotential as a function of current density is plotted in Figure 9, page 40.

Electrolyte: 0.70 N Potassium Nitrate - 0.30 N Silver Nitrate. The potential of the silver electrode undergoing anodic dissolution at temperatures of 25 and 50°C in 0.70 N potassium nitrate - 0.30 N silver nitrate solution is recorded in Tables XIII and XIV, pages 41 and 42, respectively. Figures 10 and 11, pages 43 and 44, respectively, show the relationship between the overpotential and current density. The range of current density was from zero to 0.100 amp·cm⁻². The salt bridge solution was 1.00 N ammonium nitrate.

TABLE XI

Dissolution Potential of the Silver Electrode in
 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C

I x 10 ³ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b		Overpotential (volts)	
	Run 1	Run 2	Run 1	Run 2
0.00	0.691	0.690	0.012	0.011
0.16	0.692	-	0.013	-
0.20	-	0.691	-	0.012
0.25	0.697	-	0.018	-
0.40	-	0.694	-	0.015
0.42	0.699	-	0.020	-
0.70	0.700	-	0.021	-
1.00	-	0.701	-	0.022
1.10	0.701	-	0.022	-
1.60	0.703	-	0.024	-
2.00	-	0.708	-	0.029
2.80	0.711	-	0.032	-
4.00	0.717	0.717	0.038	0.038
8.00	0.728	0.730	0.049	0.051
15.00	0.743	-	0.064	-
20.00	-	0.751	-	0.072
40.00	-	0.771	-	0.092
60.00	-	0.802	-	0.123

Calculated reversible potential = 0.679 volts

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

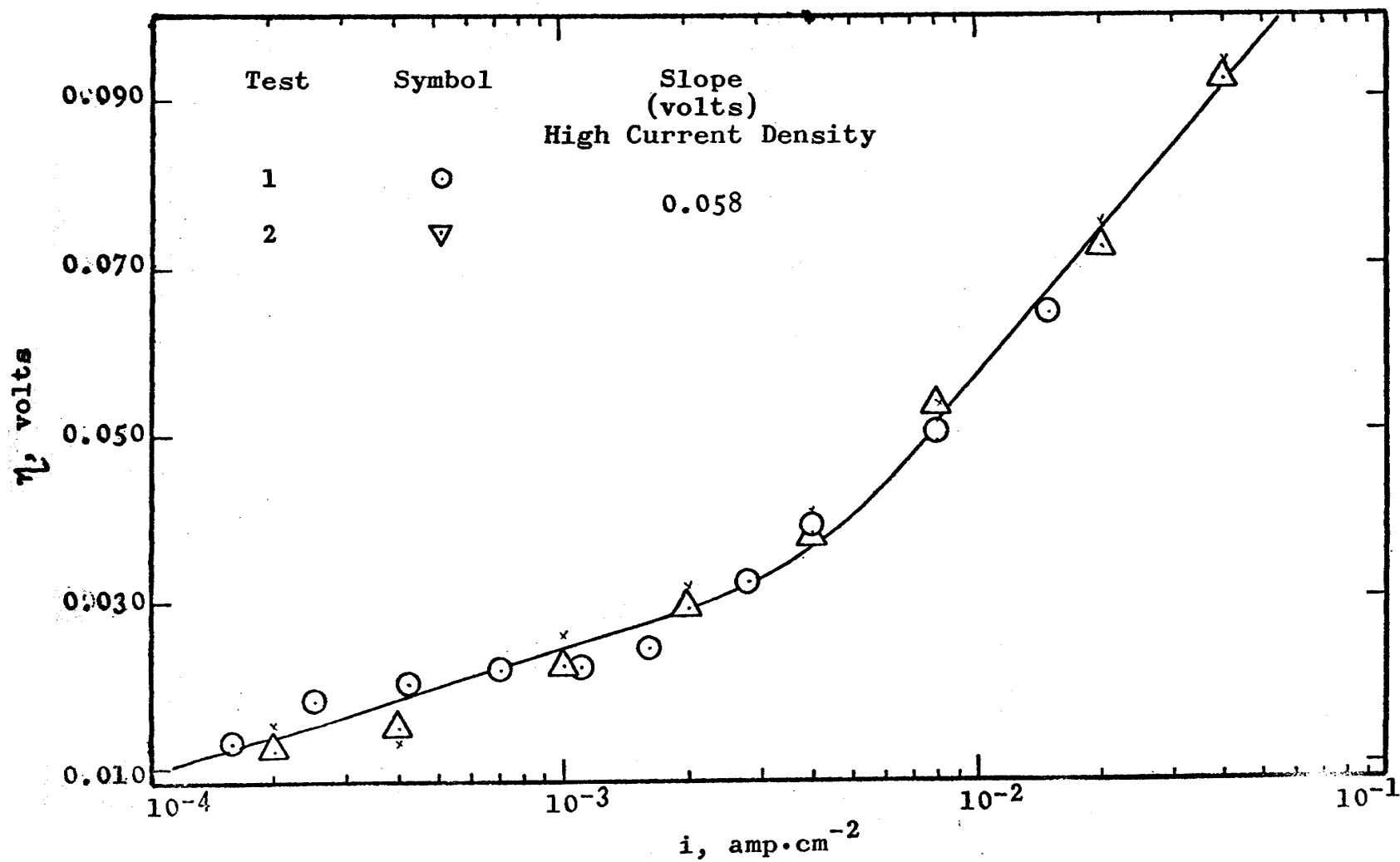


Figure 8. The Tafel curve for the anodic dissolution of silver in 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C.

TABLE XII

Dissolution Potential of the Silver Electrode in
 0.90 N KNO_3 - 0.10 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b		Overpotential (volts)	
	Run 1	Run 2	Run 1	Run 2
0.00	0.730	0.724	0.020	0.014
0.16	0.731	0.730	0.021	0.020
0.25	0.731	0.730	0.021	0.020
0.42	0.732	0.731	0.022	0.021
1.10	0.733	0.731	0.023	0.021
1.60	0.736	0.731	0.026	0.021
2.80	0.740	0.732	0.030	0.022
4.00	0.742	0.739	0.032	0.029
8.00	0.751	0.750	0.041	0.040
15.00	0.762	0.762	0.052	0.052
25.00	0.780	0.780	0.070	0.070

Calculated reversible potential = 0.710 volts

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

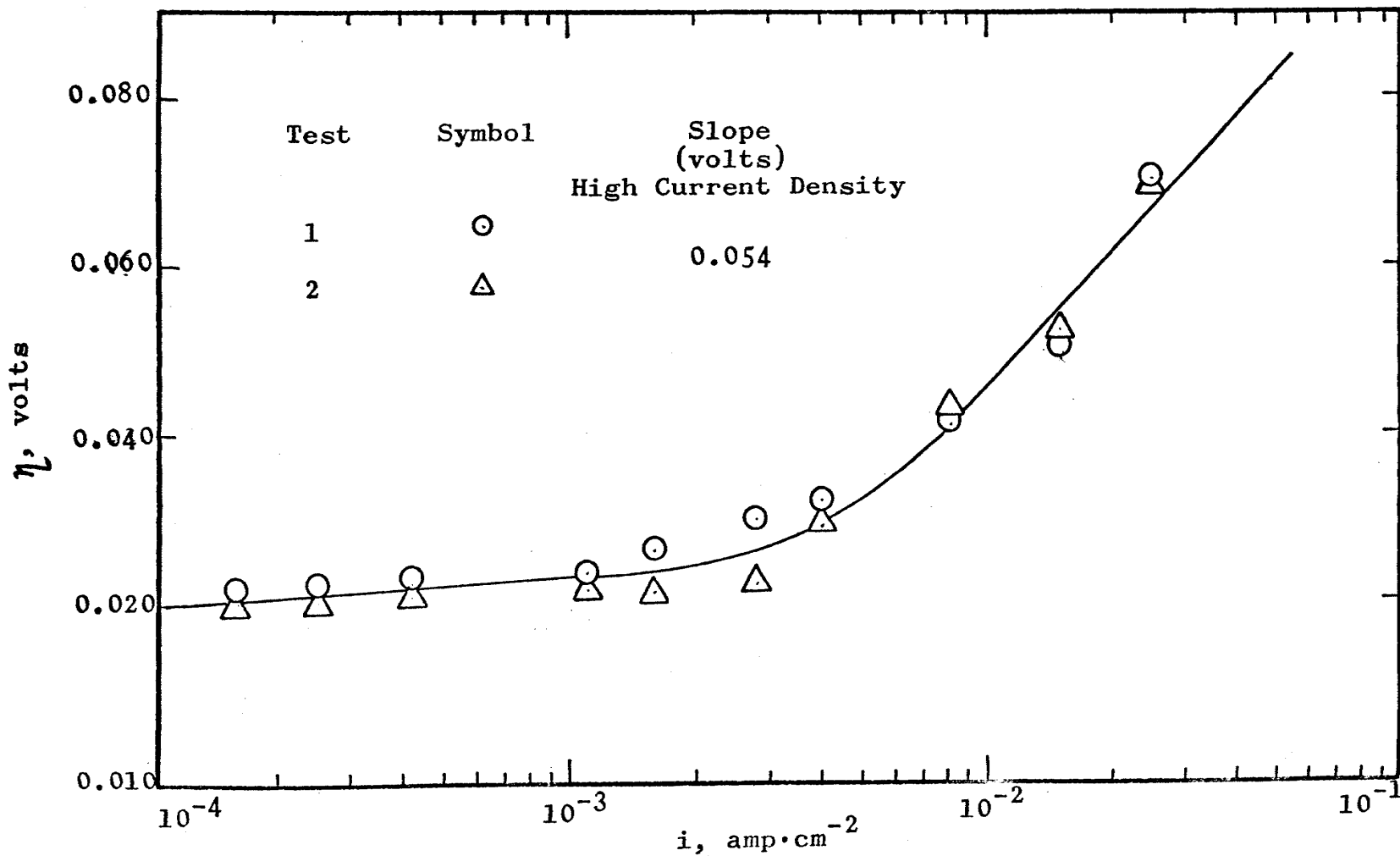


Figure 9. The Tafel curve for the anodic dissolution of silver in 0.90 N KNO_3 - 0.10 N AgNO_3 at 25°C:

TABLE XIII

Dissolution Potential of the Silver Electrode in
 0.70 N KNO_3 - 0.30 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b	Overpotential (volts)
0.00	0.746	0.008
0.20	0.750	0.012
0.40	0.751	0.013
1.00	0.752	0.014
2.00	0.753	0.015
4.00	0.758	0.020
8.00	0.760	0.022
20.00	0.762	0.024
40.00	0.771	0.033
60.00	0.781	0.043
100.00	0.792	0.054

Calculated reversible potential = 0.738 volts

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XIV
 Dissolution Potential of the Silver Electrode in
 0.70 N KNO_3 - 0.30 N AgNO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b	Overpotential (volts)
0.00	0.739	0.033
0.20	0.741	0.035
0.40	0.741	0.035
1.00	0.743	0.037
2.00	0.744	0.038
4.00	0.747	0.041
8.00	0.750	0.044
20.00	0.760	0.054
40.00	0.773	0.067
80.00	0.800 ^c	0.084 ^c

Calculated reversible potential = 0.706 volts

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

^cPotential kept increasing

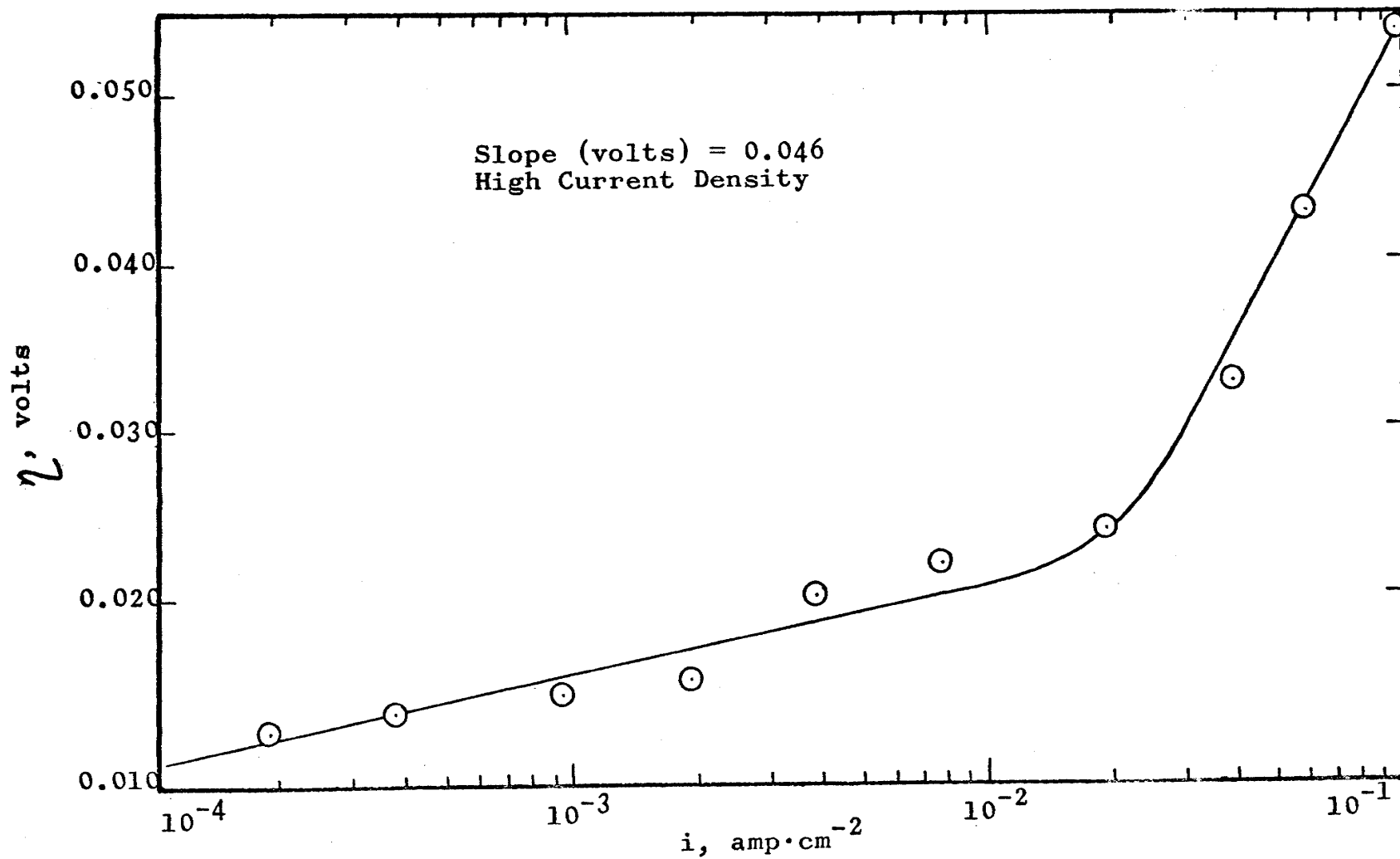


Figure 10. The Tafel curve for the anodic dissolution of silver in 0.70 N KNO_3 - 0.30 N AgNO_3 at 25°C.

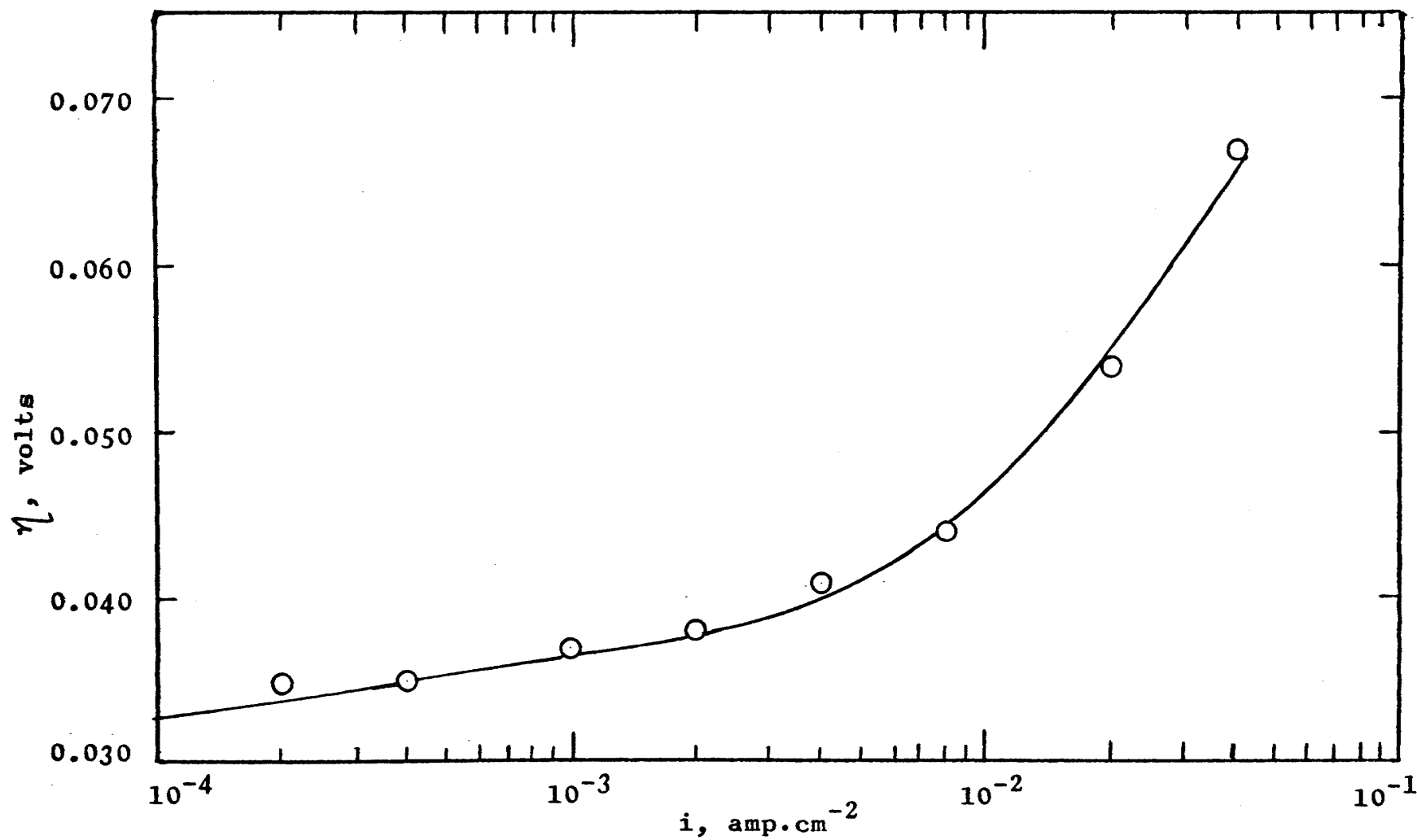


Figure 11. The Tafel Curve for the anodic dissolution of silver in 0.70N KNO_3 - 0.30N AgNO_3 at 50°C.

Electrolyte: 0.70 N Ammonium Nitrate - 0.30 N Silver Nitrate. The potential of the silver electrode as a function of current density at temperatures of 25 and 50°C in 0.70 N ammonium nitrate - 0.30 N silver nitrate solution is shown in Tables XV and XVI, pages 46 and 47, respectively. Figures 12 and 13, pages 48 and 49, show the relationship between the overpotential and current density. The range of current density was from zero to 0.080 amp·cm⁻². A salt bridge of 1.00 N ammonium nitrate was used.

Electrolyte: 1.00 N Silver Nitrate. At a temperature of 25°C, silver was dissolved anodically at various current densities in 1.00 N silver nitrate. The potential of the silver electrode was obtained at various current densities ranging between zero and 0.020 amp·cm⁻² and is shown in Table XVII, page 50. A plot of overpotential as a function of current density is shown in Figure 14, page 51. 1.00 N ammonium nitrate solution was used in the salt bridge.

Sample Calculations. The method used for the calculation of overpotentials in potassium nitrate, ammonium nitrate, mixtures of potassium nitrate and silver nitrate, and mixtures of ammonium nitrate and silver nitrate solutions was the same. The data from Table VI, page 25, have been used to illustrate the calculation involved in this part of experimentation.

TABLE XV

Dissolution Potential of the Silver Electrode in
 0.70 N NH_4NO_3 - 0.30 N AgNO_3 at 25°C

I x 10 ³ (amp·cm ⁻²) ^a	Dissolution Potential (volts) ^b		Overpotential (volts)	
	Run 1	Run 2	Run 1	Run 2
0.00	0.749	0.744	0.011	0.006
0.20	0.751	0.749	0.013	0.011
0.40	0.751	0.749	0.013	0.011
1.00	0.751	0.750	0.013	0.012
2.00	0.752	0.751	0.014	0.013
4.00	0.753	0.752	0.015	0.014
8.00	0.760	0.759	0.022	0.021
20.00	0.769	0.770	0.031	0.032
40.00	0.789	0.781	0.051	0.043
80.00	0.839 ^c	0.830 ^c	0.101 ^c	0.092 ^c

Calculated reversible potential = 0.738 volts

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

^cPotential kept increasing

TABLE XVI
 Dissolution Potential of the Silver Electrode in
 0.70 N NH_4NO_3 - 0.30 N AgNO_3 at 50°C

$I \times 10^3$ (amp.cm ⁻²) ^a	Dissolution Potential (volts)	Overpotential (volts)
0.00	0.739	0.033
0.20	0.741	0.035
0.40	0.741	0.035
1.00	0.742	0.036
2.00	0.743	0.037
4.00	0.744	0.038
8.00	0.749	0.043
20.0	0.753	0.047
40.00	0.769	0.063
80.00	0.800 ^c	0.084 ^c

Calculated reversible potential = 0.706 volts

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

^cPotential kept increasing

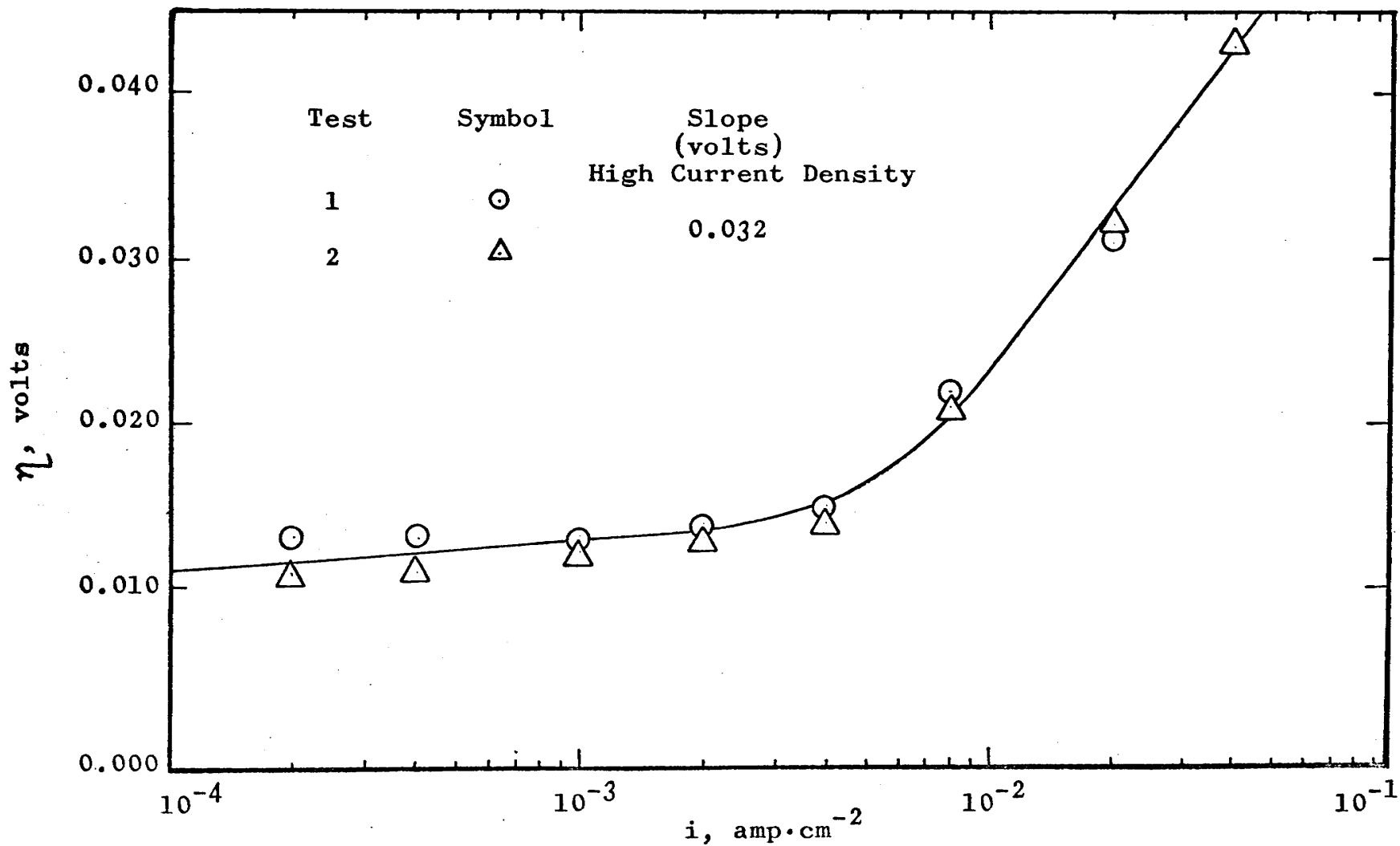


Figure 12. The Tafel curve for the anodic dissolution of silver in 0.70 N KNO₃ - 0.30 N AgNO₃ at 25°C.

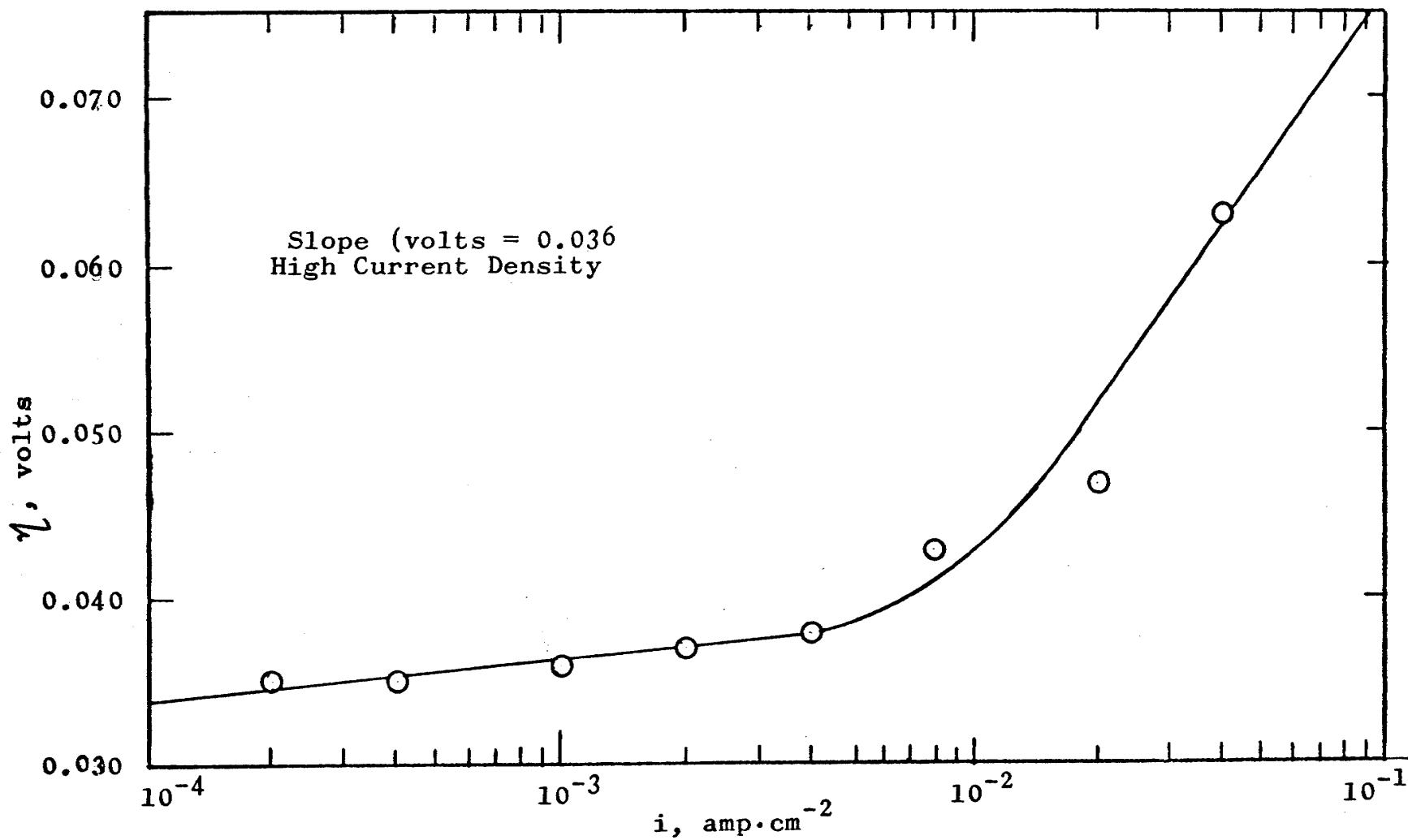


Figure 13. The Tafel curve for the anodic dissolution of silver in 0.70 NH_4NO_3 - 0.30 N AgNO_3 at 50°C.

TABLE XVII
 Dissolution Potential of the Silver Electrode in
 1.00 N AgNO₃ at 25°C

I x 10 ³ (amp·cm ⁻²)	Dissolution Potential (volts) ^a		Overpotential (volts)	
	Run 1 ^b	Run 2 ^c	Run 1	Run 2
0.00	0.781	0.791	0.004	0.014
0.16	0.789	0.799	0.012	0.022
0.25	0.790	0.800	0.013	0.023
0.42	0.790	0.801	0.013	0.024
0.70	0.791	0.801	0.014	0.024
1.10	0.791	0.801	0.014	0.024
1.60	0.791	0.802	0.014	0.025
4.00	0.792	0.811	0.015	0.034
8.00	0.799	0.820	0.020	0.043
15.00	-	0.831	-	0.054
20.00	0.809	0.841	0.032	0.064

Calculated reversible potential = 0.777 volts

^aNormal hydrogen scale

^bArea of the electrode = 0.723 cm²

^cArea of the electrode = 0.664 cm²

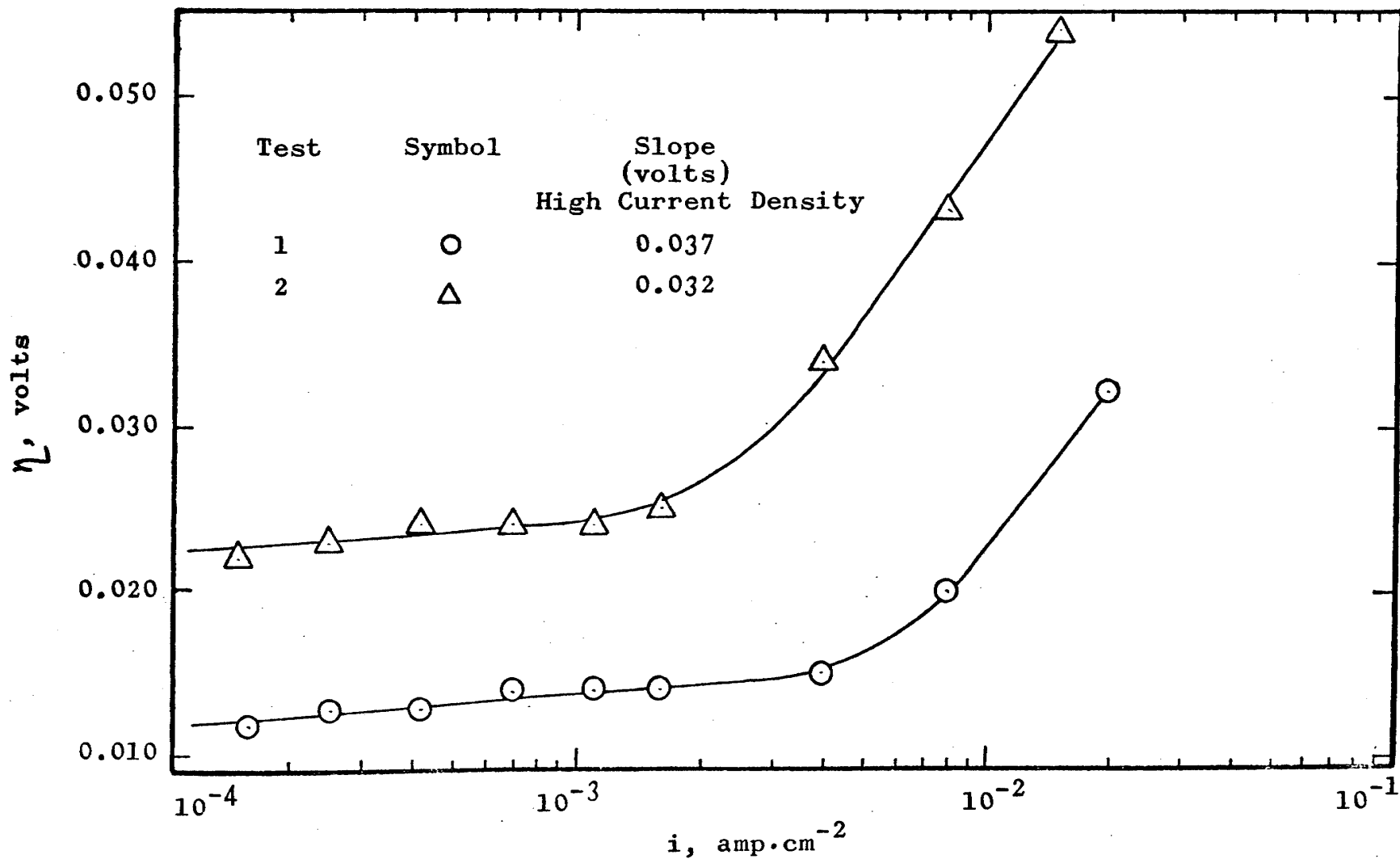


Figure 14. The Tafel curves for the anodic dissolution of silver in 1.00 N AgNO_3 at 25°C .

Calculation of the Overpotential of the Silver from Dissolution Potential Data. The overpotential of silver was calculated by means of the equation:

$$\eta = E_i - E_r \quad (10)$$

where,

η = overpotential at a current density of $0.040 \text{ amp}\cdot\text{cm}^{-2}$

E_i = steady dissolution potential at a current density of $0.040 \text{ amp}\cdot\text{cm}^{-2} = 0.792 \text{ volts}$

E_r = reversible potential of the silver electrode calculated using Nernst equation = 0.445 volts .

Therefore, $\eta = 0.792 - 0.445 = 0.347 \text{ volts}$.

Calculation of the Reversible Potential

The reversible potential of the electrode was calculated by the Nernst equation:

$$E_r = E_o - \frac{2.303 RT}{z F} \log \frac{a_{\text{Ag}}}{a_{\text{Ag}^+}} \quad (11)$$

where,

E_r = reversible potential of the silver electrode, volts

E_o = standard potential of the silver electrode
 $= 0.799 - 9.895 \times 10^{-4}(T-298)^* = 0.799 \text{ volts}$

R = gas constant = $8.314 \text{ joules/gm mole } ^\circ\text{K}$

T = temperature = 298°K

* reference (17)

$z = \text{number of charges transferred} = 1$

$F = \text{Faraday constant} = 96,500 \text{ coulombs/equivalent}$

$a_{\text{Ag}^+} = \text{activity of silver ion} = 10^{-6} \text{ (assumed)}$

Therefore,

$$\begin{aligned} E_r &= 0.799 + 0.0591 \log 10^{-6} \\ &= 0.445 \text{ volts.} \end{aligned}$$

In mixed electrolytes, the Debye-Huckel equation was used in estimating the activity of the silver ions.

The reversible potential of the silver electrode is a function of the bulk concentration of silver ions which changes in neutral salt solutions as current is passed through the silver electrode. Calculations indicate that the bulk concentration of silver ions due to the passage of a current of one milliamperere for an hour is approximately 10^{-5} moles/liter. Therefore it was assumed that the reversible potential of the silver electrode remained constant for the current densities considered and could be evaluated for an average activity of 10^{-6} moles/liter.

IV. DISCUSSION

Discussion of the results is presented in two parts: (1) anodic dissolution of silver at various temperatures, and (2) the relationship between the overpotential of the silver anode and current density, in aqueous solutions.

Anodic Dissolution of Silver in Aqueous Solutions.

The anodic dissolution of silver was studied at various temperatures in one normal solutions of potassium sulfate, potassium nitrate, and ammonium nitrate. Preliminary studies were made with the purpose of determining the Faradaic efficiency for the anodic dissolution of silver and if any deviation from Faraday's law exists.

In one normal potassium sulfate solution at a temperature of 25°C, the apparent valence of silver (Table I, page 15) is found to increase above the normal value of one with an increase in current density. This increase in the apparent valence can be explained in terms of a partial passivation of the silver surface. Gas bubbles (probably of oxygen) were observed forming on the electrode surface at current densities of 0.00147 and 0.00737 amp·cm⁻². This secondary reaction resulted in a proportionally smaller weight of silver being dissolved anodically than predicted by Faraday's law, thus causing the apparent valence to be greater than one.

It can be seen (Tables II through V, pages 16, 17, 20, and 21, respectively) that in one normal solutions of potassium nitrate and ammonium nitrate, the apparent valence of silver is close to the normal value. In potassium nitrate at 25°C, a dark-colored film was observed on the surface of the silver electrode at a current density of 0.1264 amp·cm⁻². This film was also observed on the surface at a temperature of 50°C at all current densities. After the film was formed, it remained on the surface during the entire dissolution experiment. It did not spall off the surface at any of the current densities investigated.

A similar film was also observed on the silver anode in ammonium nitrate at both temperatures (25 and 50°C) and at all current densities. Also, in ammonium nitrate, the film remained on the surface of the electrode during the dissolution process. This dark-colored film was removed from the surface with a rubber policeman and examined. It was found to contain small metallic particles of silver.

This same black film was also observed when silver was anodically dissolved in silver nitrate solution. This phenomenon has been reported by Vermilyea (6) who found an "anode slime" composed of minute particles of silver during the dissolution of silver in a normal solution of silver nitrate at a current density of 1.0 amp·cm⁻².

In potassium and ammonium nitrate solutions at 25 and 50°C, the apparent valence of silver is always slightly less than one by one to five per cent. The calculated error for the valence determinations is plus or minus one per cent. As the values of the experimentally determined valence are not scattered around a normal value, it is concluded that a slightly greater amount of silver than the Faradaic equivalence is being removed from the electrode by the current. For example, at a current density of $0.05899 \text{ amp}\cdot\text{cm}^{-2}$ four different tests were made in 1.00 N potassium nitrate at 25°C (Table II, page 16). The values obtained during the tests are within the experimental error of plus or minus one per cent. Based on the appearance of the metallic particles on the anode surface, it is also concluded that a small amount of disintegration of silver takes place during the dissolution process and this accounts for the apparent valence less than one.

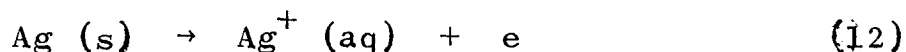
The Relationship between the Overpotential of the Silver Anode and the Current Density in Aqueous Solutions.

Overpotential measurements as a function of current density were made in various electrolytes (potassium nitrate, ammonium nitrate, potassium nitrate - silver nitrate mixture, and ammonium nitrate - silver nitrate mixture). Constant temperatures of 25 and 50°C were used. The purpose was to

study the mechanism of the anodic dissolution of silver. The concentration of silver ions in the mixed electrolytes was varied from 0.01 to 1.00 gram-equivalents per liter. The ionic strength was held constant at one gram-equivalent per liter.

The overpotentials measured in potassium nitrate and ammonium nitrate were greater than 0.100 volts even at low current densities (10^{-4} amp·cm⁻²). In mixed electrolytes, that is, potassium nitrate - silver nitrate and ammonium nitrate - silver nitrate, the overpotentials were less than 0.050 volts up to current densities of 0.010 amp·cm⁻². This indicated a possible difference in mechanism for the dissolution of silver in the different electrolytes.

In mixed electrolytes (mixture of potassium nitrate - silver nitrate), if it is assumed that the rate determining step for the dissolution of silver is the electron transfer step,



then from equation (12),

$$i^* = k_1 \theta_{\text{Ag}} \exp \left[\frac{z F \alpha \eta}{R T} \right] - \frac{k_1}{K_1} C_{\text{Ag}^+} \exp \left[\frac{-(1-\alpha) z F \eta}{R T} \right] \quad (13)$$

where,

i = current density, amp·cm⁻²

θ = fractional surface coverage

α = symmetry factor, assumed to be 0.5

k = rate constant

K = equilibrium constant

F = Faraday constant = 96,500 coulombs/equivalent

z = number of charges transferred = 1

η = overpotential, volts

R = gas constant = 8.314 joules/gm mole $^{\circ}\text{K}$

T = temperature, $^{\circ}\text{K}$.

Since the irreversibility of the electrode process is small ($\eta < 0.050$ volts approximately), the exponential terms in equation (13) may be expanded using the approximate relation,

$$\exp(x) = 1 + x \quad (14)$$

Therefore,

$$i = k_1 \theta_{\text{Ag}} \left(1 + \frac{\alpha F \eta}{R T}\right) - \frac{k_1}{K_1} C_{\text{Ag}^+} \left[1 - \frac{(1 - \alpha) F \eta}{R T}\right] \quad (15)$$

or,

$$i = k_1 \theta_{\text{Ag}} \left(1 + \frac{F \eta}{2 R T}\right) - \frac{k_1}{K_1} C_{\text{Ag}^+} \left(1 - \frac{F}{2 R T}\right). \quad (16)$$

Equation (16) can be simplified to

$$\eta = \frac{2 R T}{k_1 F} \left(\frac{K_1}{K_1 \theta_{\text{Ag}} + C_{\text{Ag}^+}}\right) i - \frac{2 R T}{F} \left(\frac{K_1 \theta_{\text{Ag}} - C_{\text{Ag}^+}}{K_1 \theta_{\text{Ag}} + C_{\text{Ag}^+}}\right) \quad (17)$$

If the overpotential is plotted as a function of current density, then from equation (17),

$$\text{slope} = \frac{2 R T}{k_1 F} \left(\frac{K_1}{K_1 \theta_{Ag} + C_{Ag^+}} \right) \quad (18)$$

and,

$$\text{intercept} = - \frac{2 R T}{F} \left(\frac{K_1 \theta_{Ag} - C_{Ag^+}}{K_1 \theta_{Ag} + C_{Ag^+}} \right). \quad (19)$$

The equilibrium constant, K_1 , for reaction (12) cannot be evaluated thermodynamically. Since silver is a noble metal having a small tendency to oxidize to silver ions, K_1 can be assumed small. Also, θ_{Ag} is less than or equal to one. If (and it is probable) $K_1 \theta_{Ag} < C_{Ag^+}$, then the slope and the intercept will be approximated by $\frac{2 R T}{k_1 F} \frac{K_1}{C_{Ag^+}}$ and $\frac{2 R T}{F}$, respectively, from equations (18) and (19). Therefore the slope should be proportional to the temperature at a constant concentration of silver ions and should be inversely proportional to the concentration of silver ions at constant temperature. Similarly, at constant temperature the intercept should be independent of silver ion concentration. Figures 15 through 19, pages 60 through 64, are plots of overpotential versus current density for different electrolytes. Experimental values of slopes and intercepts (Table XVIII, page 65) are plotted (Figure 20, page 66) as a function of silver ion concentration. It can be seen from

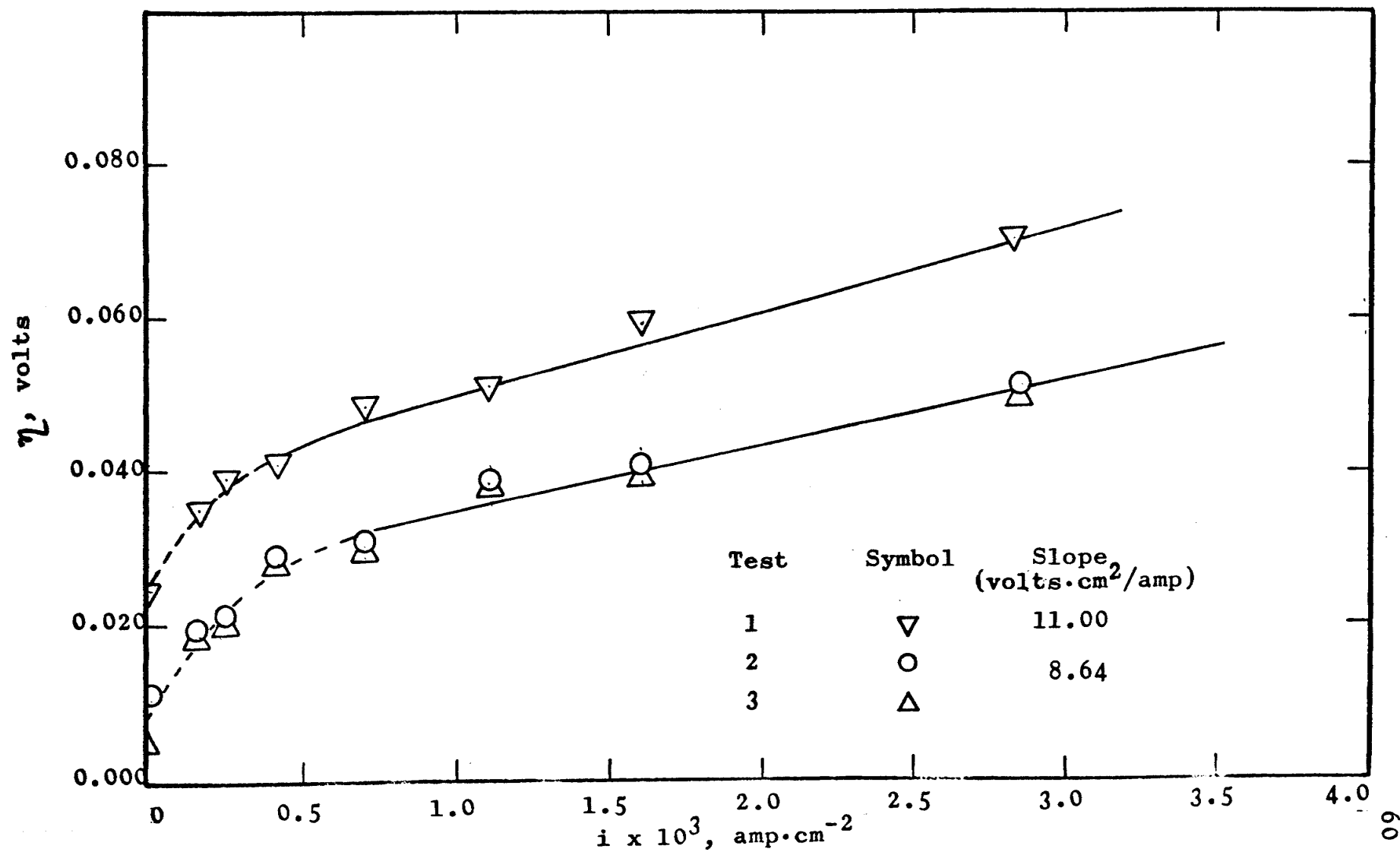


Figure 15. Anodic behavior of silver at low overpotentials in 0.99 N KNO₃ - 0.01 N AgNO₃ at 25°C.

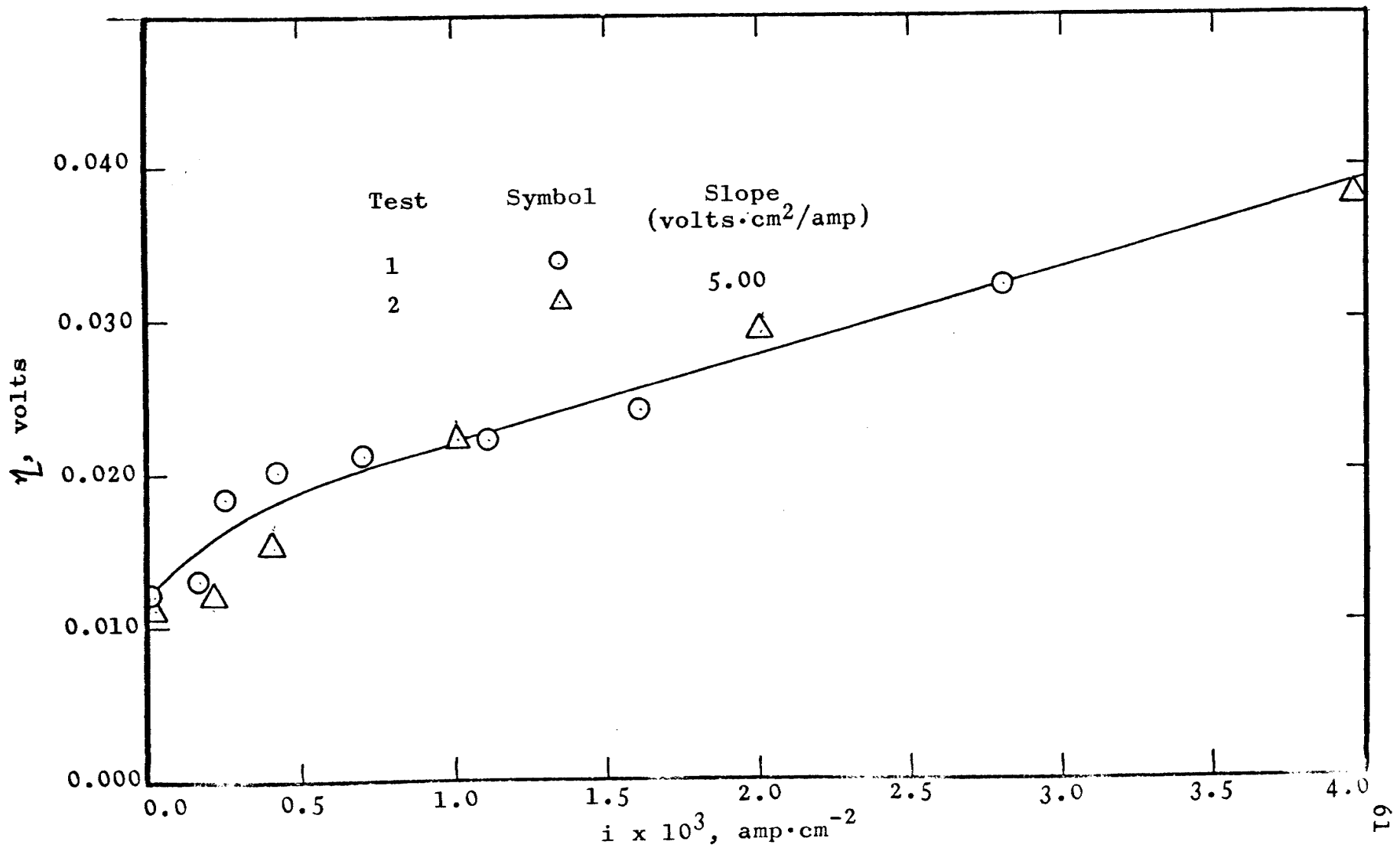


Figure 16. Anodic behavior of silver at low overpotentials in 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C.

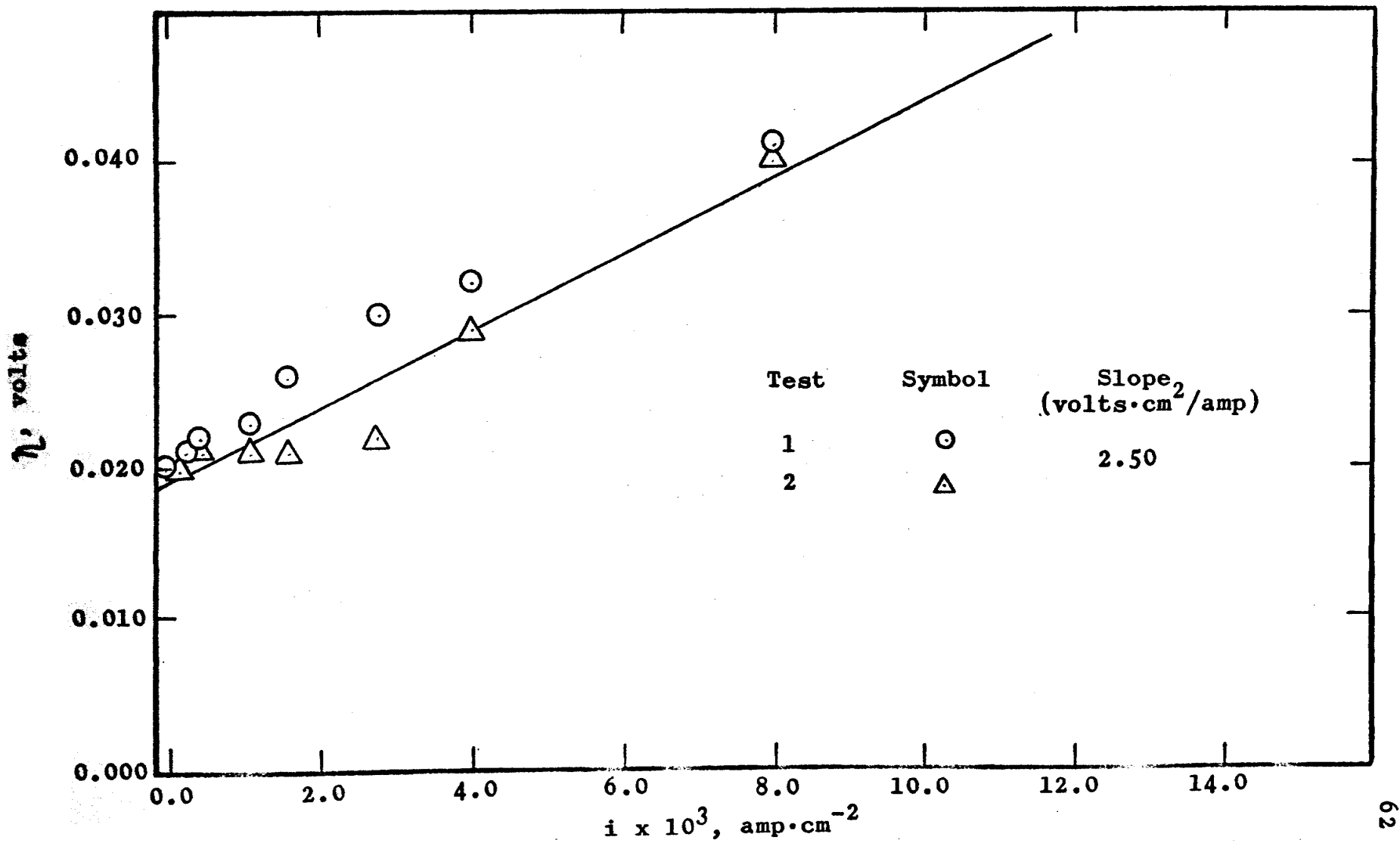


Figure 17. Anodic behavior of silver at low overpotentials in 0.90 N KNO₃ - 0.10 N AgNO₃ at 25°C.

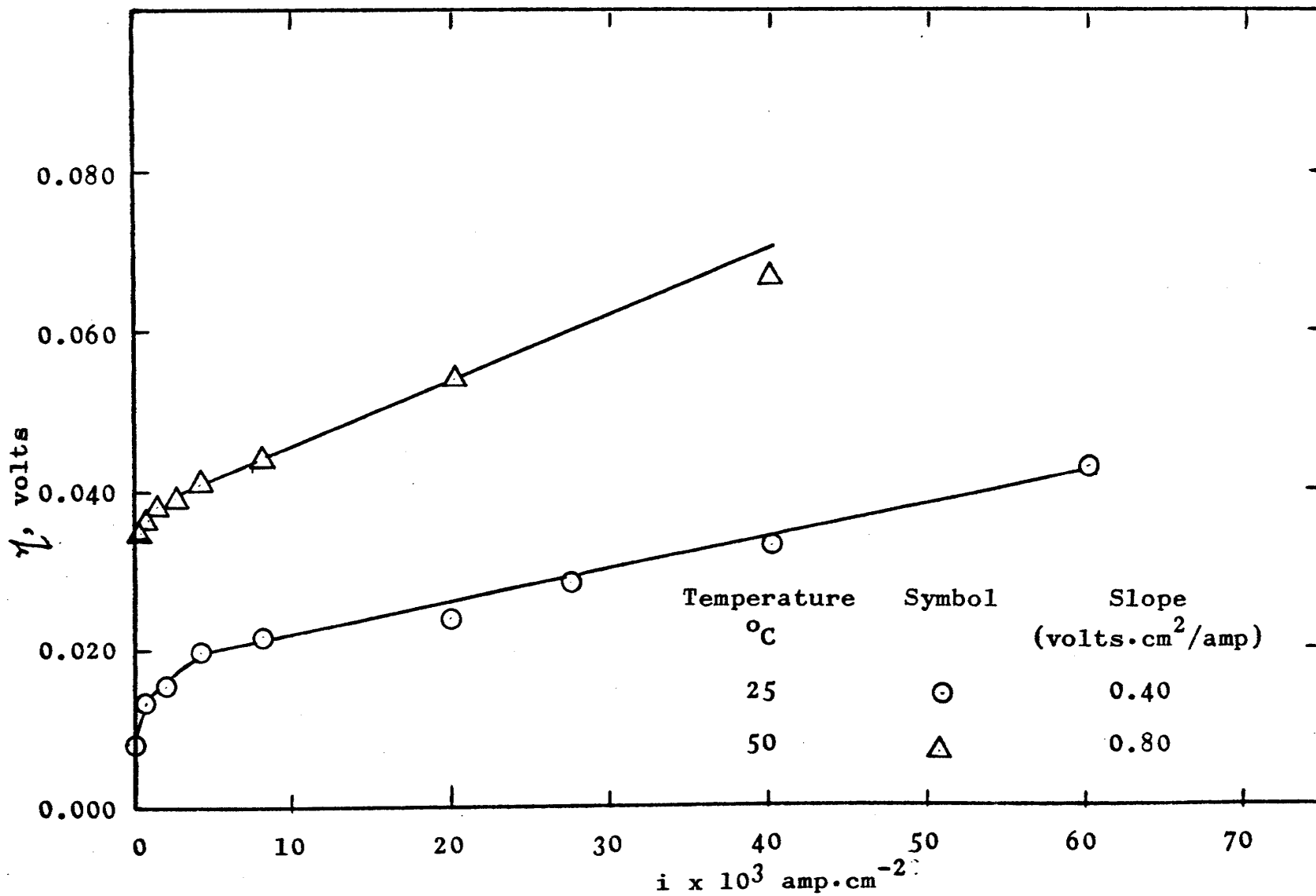


Figure 18. Anodic behavior of silver at low overpotentials in 0.70N KNO₃ - 0.30N AgNO₃ at 25 and 50°C.

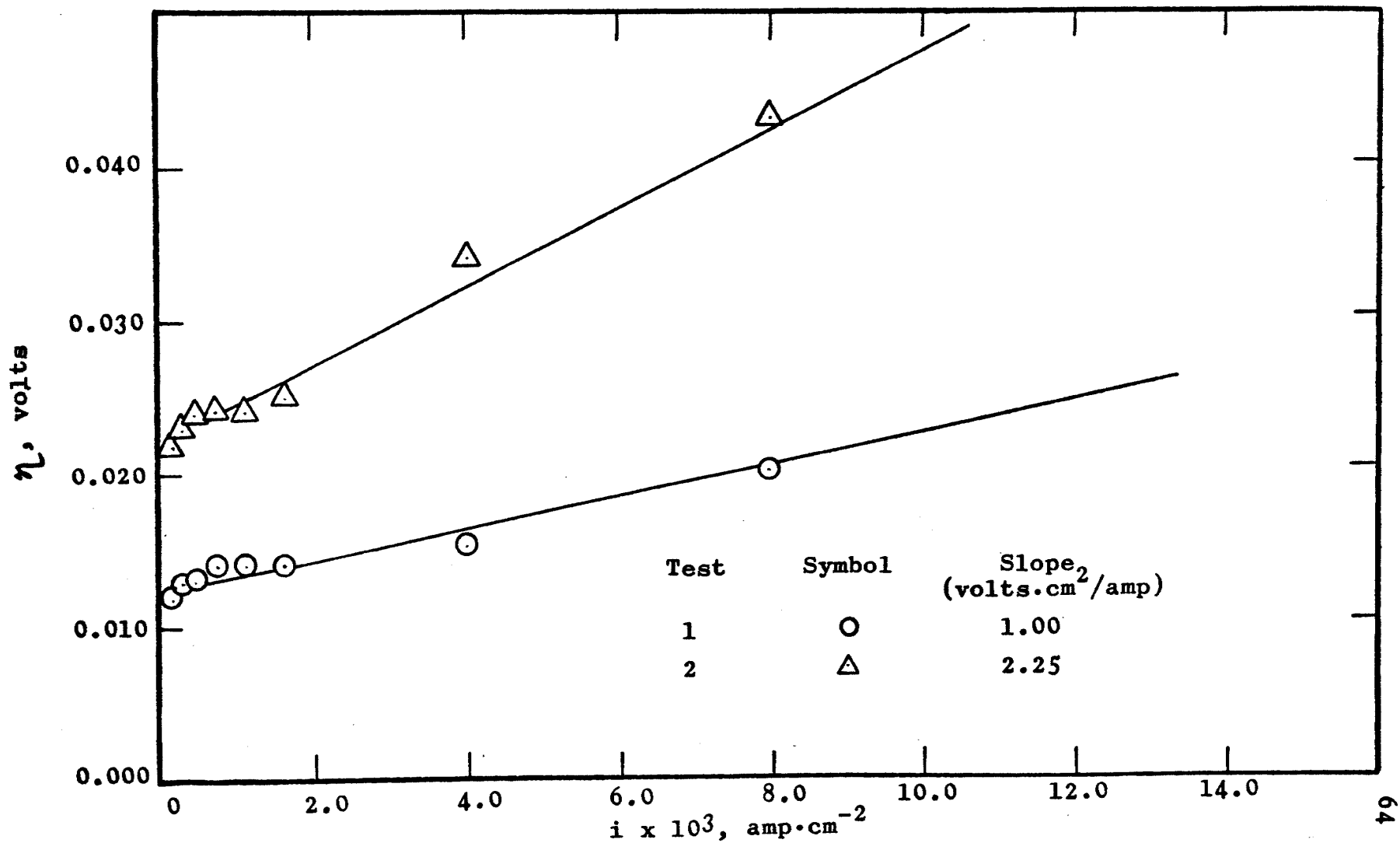


Figure 19. Anodic behavior of silver at low overpotentials in 1.00 N AgNO₃ at 25°C.

TABLE XVIII
Parameters of Tafel Curves

Electrolyte			Temp.	Slope* vs. i	Inter- cept	Slope* vs. log i	Exchange Current Density	Reversible	Potential Rest			
<u>gm-equivalent</u> liter			°C	<u>volt·cm²</u> amp	volts	volts	amp·cm ⁻²		volts**			
AgNO ₃	KNO ₃	NH ₄ NO ₃							Run 1	Run 2	Run 3	Run 4
0.00	1.00	0.00	25	-	-	0.060	10 ⁻⁶ to 10 ⁻⁸	0.445	0.463	0.447	-	-
0.00	1.00	0.00	50	-	-	0.073	10 ⁻⁶	0.390	0.447	0.446	-	-
0.00	0.00	1.00	25	-	-	0.062	10 ⁻⁶ to 10 ⁻⁷	0.445	0.369	0.396	0.461	0.476
0.00	0.00	1.00	50	-	-	0.070	10 ⁻⁶	0.390	0.433	0.337	-	-
0.01	0.99	0.00	25	9.82	0.030	0.051	10 ⁻⁴	0.651	0.676	0.656	0.661	-
0.03	0.97	0.00	25	5.00	0.016	0.058	10 ⁻³ to 10 ⁻⁵	0.679	0.691	0.690	-	-
0.10	0.90	0.00	25	2.50	0.018	0.054	10 ⁻⁴	0.710	0.730	0.724	-	-
0.30	0.70	0.00	25	0.40	0.017	0.046	10 ⁻³	0.738	0.746	-	-	-
0.30	0.70	0.00	50	0.80	0.038	-	10 ⁻³	0.706	0.739	-	-	-
0.30	0.00	0.70	25	-	-	0.032	10 ⁻²	0.738	0.749	0.744	-	-
0.30	0.00	0.70	50	-	-	0.036	10 ⁻²	0.706	0.739	-	-	-
1.00	0.00	0.00	25	1.62	0.017	0.034	10 ⁻³	0.777	0.781	0.791	-	-

* Average value

** Normal hydrogen scale

*** Reference 20

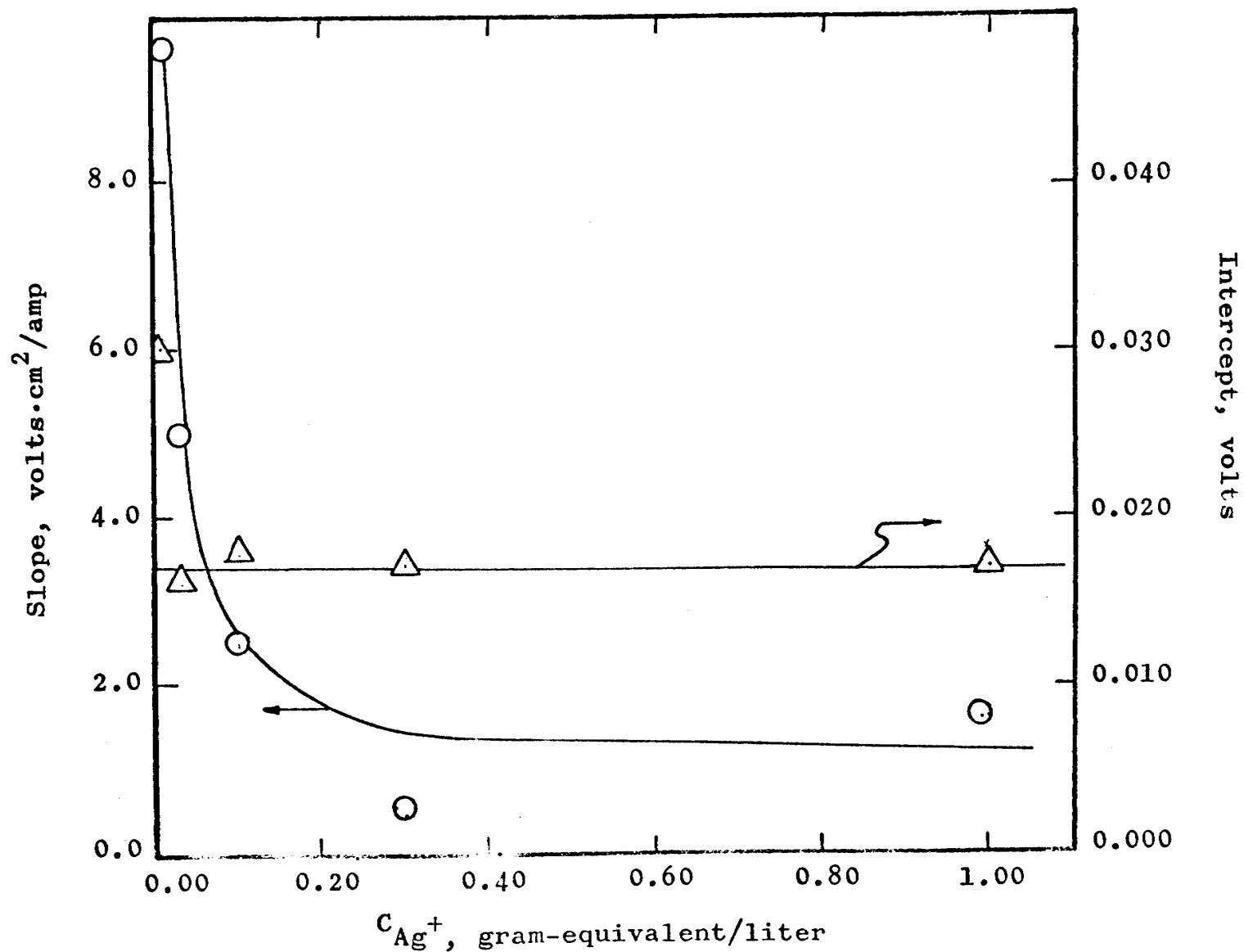


Figure 20. Concentration dependence of slope and intercept of η - i relationship for silver dissolution at low overpotentials.

the figure (Figure 20, page 66) that (very roughly) the slopes are inversely proportional to and the intercepts are independent of silver ion concentration. Experimentally, for the mixed electrolyte, 0.70 N KNO_3 - 0.30 N AgNO_3 , the slope increases from 0.40 to 0.80 volts $\cdot\text{cm}^2/\text{amp}$ with an increase in temperature from 25 to 50°C. The experimental values of the intercepts are close to 0.017 volts, except for the electrolyte, 0.99 N KNO_3 - 0.01 N AgNO_3 , for which it is 0.030 volts. The theoretical value of the intercept, $\frac{2 R T}{F}$, equals 0.051 volts. This proposed mechanism is in qualitative agreement with the experimental results at lower overpotentials.

At high overpotentials ($\eta > 0.050$ volts), the rate of the reverse reaction, see equation (12), is small compared to the rate of the forward reaction. Therefore, from equation (13),

$$i = k_1 \theta_{\text{Ag}} \exp\left(\frac{\alpha F \eta}{R T}\right) \quad (20)$$

or,

$$\eta = 2.303 \left(\frac{2 R T}{F}\right) \log i - 2.303 \left(\frac{2 R T}{F}\right) \log k_1 \theta_{\text{Ag}} \quad (21)$$

When overpotential is plotted as a function of the logarithm of current density, the experimental values of the slopes are close to 0.060 volts instead of 0.120 volts as predicted.

This indicates a possible difference in mechanism at higher overpotentials compared to the simple electron transfer at low overpotentials. Also, in the mixed electrolyte, as the overpotential increased above 0.050 volts, there is an apparent discontinuity in the Tafel curves (Figures 7 through 11, and 14, pages 35, 38, 40, 43, 44, and 51, respectively). This is another indication of the possible difference in mechanism that may exist between the low and high overpotential regions. It should be kept in mind that it was only in solutions containing no silver ions that overpotentials much greater than 0.050 volts were reached.

The rest potential of the electrode in electrolytes (Table XVIII, page 65) containing silver ions is close to the calculated reversible potential, but in potassium nitrate and ammonium nitrate, it lies between the reversible potentials of the Ag/AgO (18) and Ag/Ag⁺ electrodes and is closer to the latter. These rest potentials were not reproducible. This may be because of a partial coverage of oxide film on the surface of the electrode. At high current density (approximately 0.10 amp·cm⁻²), the potential of the silver anode kept increasing indicating a passivation of the electrode. Silver oxide has been reported (identified by x-ray analysis) to exist on the surface of silver anodes in acid solution (2N H₂SO₄) prior to oxygen evolution at a current density of 0.040 amp·cm⁻² (7). This oxide is known to be a good electrical conductor (7). Based on these facts, if it

is assumed that the coverage of oxide film is small at a low current density and linearly increases to one as the current density is increased to $0.10 \text{ amp}\cdot\text{cm}^{-2}$, then,

$$\theta_{\text{AgO}} = (0.1 + 9.0 i) \quad (22)$$

or,

$$\theta_{\text{Ag}} = 1 - \theta_{\text{AgO}} = 0.9 - 9.0 i \quad (23)$$

where,

θ = fractional surface coverage

i = current density, $\text{amp}\cdot\text{cm}^{-2}$.

It is assumed here that no dissolution of silver takes place where the surface is covered with oxide film. Substituting equation (23) into equation (20) gives,

$$\eta = 2.303 \left(\frac{2R}{F} \right) \log \frac{i}{1 - 10i} - 2.303 \left(\frac{2R}{F} \right) \log 0.9 k_1 \quad (24)$$

For the electrolyte, $0.97 \text{ N KNO}_3 - 0.03 \text{ N AgNO}_3$, overpotentials are plotted as a function of $\log \frac{i}{1 - 10i}$ (Figure 21, page 71). The experimental and theoretical values of the slope are not in agreement.

Another possible mechanism is:

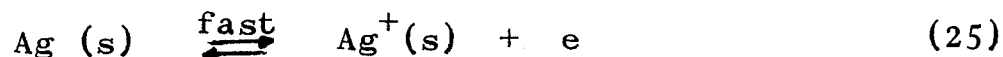


TABLE XIX

Overpotential as a Function of $\log i/(1 - 10 i)$ for the
 Electrolyte 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C

$i \times 10^3$ (amp·cm ⁻²) ^a	$1 - 10 i$	$\frac{i}{1 - 10 i} \times 10^3$ (amp·cm ⁻²)	η (volts)
1.40	0.986	1.42	0.010
2.00	0.980	2.04	0.020
3.10	0.969	3.20	0.030
4.70	0.953	4.94	0.040
10.15	0.899	11.30	0.060
25.00	0.750	33.30	0.080

^aArea of the electrode = 0.664 cm²

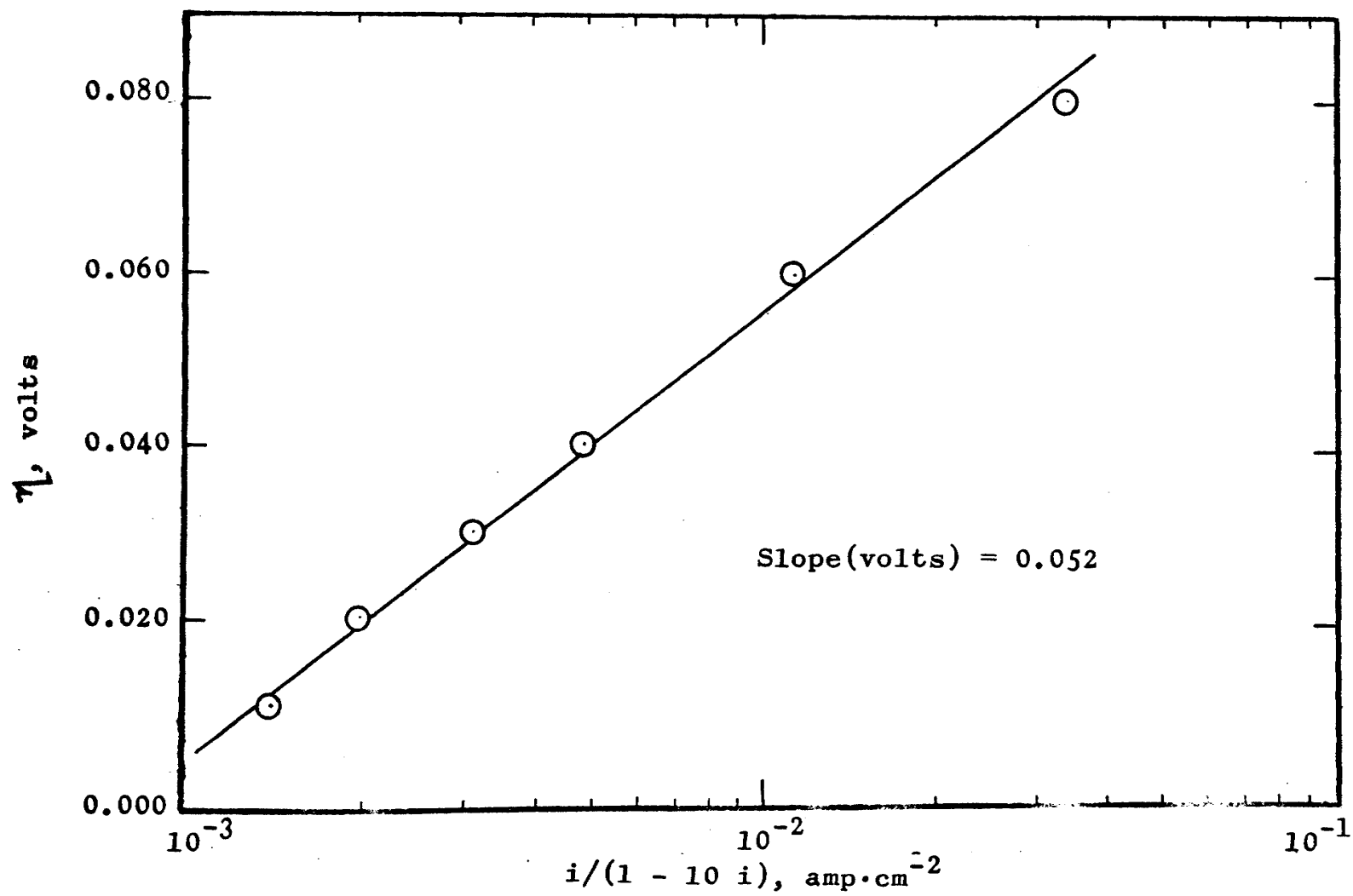


Figure 21. Overpotential as a function of $\log i/(1 - 10 i)$ for the electrolyte 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C.

In this mechanism it is assumed that a silver oxide film exists on the electrode surface and that silver underneath the film of AgO is oxidized to silver ions. The silver ion at the silver-silver oxide interface is exchanged with an ion in the oxide film and the latter is released into the solution. Thus, the oxide film (AgO) remains on the surface of the electrode and the net anodic process is the dissolution of silver. The rate expressions for equations (25) and (26), respectively, are,

$$i = \bar{k}_1 \theta_{Ag} \exp\left(\frac{-F\eta}{RT}\right) - \frac{\bar{k}_1}{K_1} \theta_{Ag^+} \exp\left(\frac{-(1-\alpha)F\eta}{RT}\right) \quad (27)$$

and,

$$i = k_2 \theta_{Ag^+} \theta_{AgO} - \frac{k_2}{K_2} C_{Ag^+} \theta_{AgO} \quad (28)$$

Assuming reaction (26) to be the rate determining step, reaction (25) can be considered at equilibrium. Therefore from equation (27),

$$\theta_{Ag^+} = \bar{K}_1 \theta_{Ag} \exp\left(\frac{F\eta}{RT}\right) \quad (29)$$

Substituting equation (29) into equation (28) gives,

$$i = k_2 \bar{K}_1 \theta_{Ag} \theta_{AgO} \exp\left(\frac{F\eta}{RT}\right) - \frac{k_2}{K_2} \theta_{AgO} C_{Ag^+} \quad (30)$$

or,

$$i = k_2 \bar{K}_1 \theta_{Ag} \exp\left(\frac{F\eta}{RT}\right) - \frac{k_2}{K_2} C_{Ag^+} \quad \left(\text{assuming } \theta_{AgO} = 1\right) \quad (31)$$

At low overpotentials, equation (31) reduces to,

$$i = k_2 \bar{K}_1 \theta_{Ag} \left(1 + \frac{F\eta}{RT}\right) - \frac{k_2}{K_2} C_{Ag^+} \quad (32)$$

Therefore,

$$\eta = \frac{RT}{F} \left(\frac{1}{k_2 \bar{K}_1 \theta_{Ag}}\right) i + \frac{RT}{F} \frac{C_{Ag^+}}{k_2 \bar{K}_1 \theta_{Ag}} - \frac{RT}{F} \quad (33)$$

Experimentally, it is found that the slope of η versus i is a function of the concentration of silver ions (see Figure 20, page 66), indicating no agreement with this mechanism at low overpotentials.

At high overpotentials, equation (31) reduces to,

$$i = k_2 \bar{K}_1 \theta_{Ag} \exp\left(\frac{F\eta}{RT}\right) \quad (34)$$

or,

$$\eta = 2.303 \left(\frac{RT}{F}\right) \log i - 2.303 \left(\frac{RT}{F}\right) \log k_2 \bar{K}_1 \theta_{Ag} \cdot \quad (35)$$

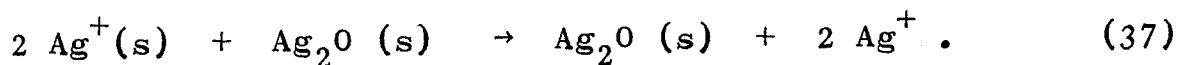
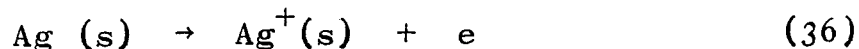
The slopes evaluated for high overpotentials (see Table XVIII, page 65) in ammonium nitrate, potassium nitrate, and in mixed electrolytes (mixtures of potassium nitrate -

silver nitrate) are close to 0.060 volts, that is, $\frac{2.303 RT}{F}$. In potassium nitrate and ammonium nitrate, the value of the slope increases approximately 0.010 volts with an increase in temperature from 25 to 50°C. Therefore, this mechanism fits quite well at high overpotentials.

Another possible mechanism combining the electron transfer and chemical reactions was considered. It was assumed that the surface of the electrode remained partially covered with the oxide film even at high current densities and that reactions (25) and (26) took place simultaneously. The final expression derived for the above mechanism did not fit the data.

It was therefore, assumed that at low overpotentials ($\eta < 0.050$ volts), the electron transfer step is rate determining and at high overpotentials ($\eta > 0.050$ volts), dissolution of silver is chemically controlled.

In 0.70 N NH_4NO_3 - 0.30 N AgNO_3 , the slope of the Tafel curve in the high overpotential region was approximately 0.030 volts. This slope can be explained by a mechanism similar to that proposed above except involving Ag_2O on the surface rather than AgO , that is,



It has been reported in the literature (5) that this type of oxide film (Ag_2O) does exist on silver electrodes in basic solutions. Because of limited data it is difficult to say anything conclusively about this reaction.

In mixed electrolytes containing silver ions, as well as in 1.00 N silver nitrate, exchange currents were on the order of 10^{-3} to 10^{-4} amp \cdot cm $^{-2}$ (see Table XVIII, page 65). This shows that the silver/silver ion electrode behaves much as a non-polarizable electrode. Except for the unpredictable value of the potential, it might find use as a reference electrode.

Accuracy and Reproducibility.

For valence measurements the accuracy of the results depended on the measurements of the current, time of electrolysis, and the analytical determination of dissolved silver. The time for the electrolysis experiments was recorded within plus or minus one second, giving an error of ± 0.5 per cent. The accuracy of the current measured depended on the scale of the milliammeter. It was ± 0.002 , ± 0.02 , and ± 0.2 milliamperes for full scale deflection of 1.5, 15, and 150 milliamperes, respectively, and could be conservatively estimated at ± 2.0 per cent. Similarly for the potential measurement, the accuracy of the electrometer was ± 0.003 volts for full scale deflection of one volt.

Reproducibility for the valence measurements was within plus or minus one per cent. In the case of potential measurements, reproducibility was within plus or minus 0.010 volts. The potential of the electrode depended on the surface preparation, etching, and the flow rate of nitrogen bubbling through the electrolyte. A constant flow rate was used throughout the experiments.

Limitations.

Because of the high resistance of the stop-cock in the electrolytic cell, valence and potential studies were limited to current densities less than $0.10 \text{ amp}\cdot\text{cm}^{-2}$.

Recommendations.

It is recommended that valence studies under the present experimental conditions be made at higher current densities (0.5 to $1.0 \text{ amp}\cdot\text{cm}^{-2}$) and at temperatures greater than 50°C to see if further disintegration of silver occurs.

The mechanism of anodic dissolution of silver in ammonium nitrate - silver nitrate mixture should be further studied for comparison with the proposed mechanism. It would also be desirable to make valence measurements in the presence of the silver ions. This could be done using a direct technique by which the weight loss of the electrode

is determined. A study of the dissolution process in the presence of trace amounts of other ions (such as Cl^- , $\text{SO}_4^{=}$, MnO_4^-) might be of interest.

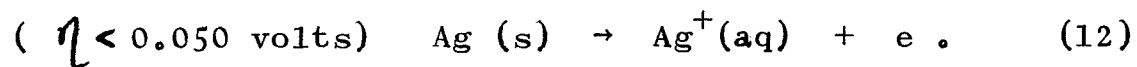
V. SUMMARY AND CONCLUSIONS

The purpose of this investigation was to study the apparent valence of silver at various current densities and the mechanism for the anodic dissolution of silver in aqueous solutions.

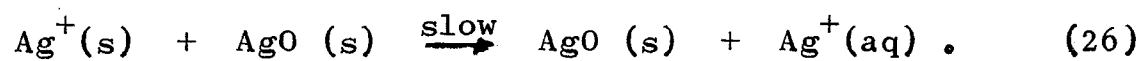
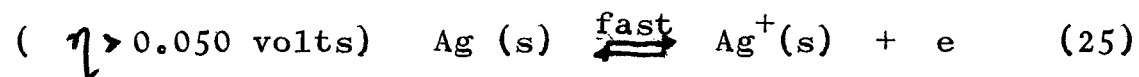
The apparent valence of silver was determined in one normal solutions of potassium nitrate and ammonium nitrate at temperatures of 25 and 50°C and in one normal potassium sulfate at 25°C. The current density was varied from 10^{-3} to 10^{-1} amp·cm⁻². The apparent valence of silver ranged between 0.95 and 1.00 in potassium nitrate and ammonium nitrate at all current densities. The amount of disintegration was quite small. In potassium sulfate the apparent valence increased with an increase in current density due to simultaneous evolution of oxygen on the electrode.

The mechanism for the anodic dissolution of silver was studied in potassium nitrate, ammonium nitrate, and in mixed electrolytes (mixtures of potassium nitrate - silver nitrate and ammonium nitrate - silver nitrate). The concentration of silver ions in the mixed electrolytes was varied from 0.01 to 1.0 gram-equivalent/liter, keeping the ionic strength constant at one gram-equivalent/liter. In potassium nitrate - silver nitrate mixture at low overpotentials ($\eta < 0.050$ volts approximately), the rate determining step

is proposed as the electron transfer step.



At high overpotentials the dissolution seems to be chemically controlled:



VI. APPENDICES

Three appendices are included in this thesis.

Appendix A contains a list of materials used in this investigation. Appendix B contains a procedure for the surface preparation of silver specimens. Appendix C contains the time behavior of the dissolution potential of the silver electrode in various electrolytes.

APPENDIX A

Materials

The following is a list of the major materials used in this investigation:

1. Potassium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.
2. Potassium Nitrate. Reagent grade, meets ACS specifications. General Chemical Company, New York, N.Y.
3. Ammonium Nitrate. Reagent grade, meets ACS specifications. Malinckrodt Chemical Works, St. Louis, Missouri.
4. Silver Nitrate. Reagent grade, meets ACS specifications. Matheson Coleman and Bell, East Rutherford, N.J.
5. Potassium Chloride. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.
6. Sodium Chloride. Reagent grade, Fisher Scientific Company, Fair Lawn, N.Y.
7. Mercurous Chloride. Reagent grade, meets ACS specifications. Merck and Company Inc., Rahway, N.J.
8. Silver. 99.99⁺ per cent purity, Asarco, Central Research Lab., American Smelting and Refining Company, South Plainfield, N.J.

EquipmentSurface Preparation of Silver Specimen

1. Belt Surfacer. Buehler No. 1250, Buehler Ltd., Evanston, Illinois
2. Hand Grinder. Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Evanston, Illinois

Apparatus For the Electrolysis and Potential Measurements

1. Power Supply. Model 711 A, Dc regulated voltage (0 to 500 volts); Hewlett-Packard Company, Loveland, Colorado
2. Electrometer. Model 610 B, Keithley Instruments, Inc., Cleveland, Ohio
3. Ammeter. Model 931, Weston Electric Instrument Corporation, Newark, N.J.

APPENDIX B

Surface Preparation of Silver Specimens

The following procedure was used for the silver metal surface preparation:

1. All pits and irregularities were removed from the metal surface with a wet belt surfacer equipped with a No. 150 grit abrasive cloth belt.
2. The sample surface was finished on a water flushed four stage hand grinder equipped with Nos. 240, 320, 400, and 600 abrasive strips, proceeding from the coarsest to the finest.
3. The sample was rinsed with distilled water.
4. The surface was etched in dilute nitric acid and again rinsed with distilled water.

APPENDIX C

Time Behavior of the Dissolution Potential of the
Silver Electrode in Various Electrolytes

TABLE XX

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N KNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.491	2.00	0	0.689
0.00	15	0.478	2.00	25	0.689
0.00	30	0.471	2.00	40	0.690
0.00	45	0.470	2.00	55	0.690
0.00	75	0.468			
0.00	90	0.468	4.00	0	0.700
0.00	105	0.468	4.00	15	0.701
0.00	120	0.464	4.00	30	0.700
0.00	135	0.463	4.00	65	0.700
0.00	150	0.463			
			8.00	0	0.720
0.20	0	0.592	8.00	15	0.720
0.20	15	0.599	8.00	30	0.721
0.20	30	0.601	8.00	45	0.721
0.20	45	0.601			
			20.00	0	0.753
0.40	0	0.610	20.00	15	0.760
0.40	15	0.610	20.00	60	0.761
0.40	30	0.616	20.00	75	0.761
0.40	55	0.642			
0.40	70	0.639	40.00	0	0.785
0.40	85	0.651	40.00	15	0.790
0.40	100	0.652	40.00	30	0.792
0.40	120	0.660	40.00	45	0.792
0.40	135	0.660			
0.40	150	0.660	80.00	0	0.840
			80.00	20	0.860
1.00	0	0.672	80.00	35	0.871
1.00	15	0.672	80.00	55	0.880
1.00	30	0.672			

^aArea of the electrode = 0.608 cm²

^bNormal hydrogen scale

TABLE XXI

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N KNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.395	4.00	0	0.689
0.00	15	0.441	4.00	15	0.691
0.00	30	0.446	4.00	30	0.691
0.00	45	0.447			
0.00	60	0.447	8.00	0	0.711
			8.00	15	0.716
0.20	0	0.611	8.00	30	0.716
0.20	15	0.610			
0.20	30	0.610	20.00	0	0.726
			20.00	15	0.726
0.40	0	0.626	20.00	30	0.726
0.40	15	0.626			
0.40	35	0.626	40.00	0	0.761
			40.00	15	0.761
1.00	0	0.651	40.00	30	0.761
1.00	15	0.651	40.00	45	0.761
1.00	30	0.651			
2.00	0	0.671			
2.00	15	0.671			
2.00	30	0.671			

^aArea of the electrode = 0.608 cm²

^bNormal hydrogen scale

TABLE XXII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N KNO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.443	4.00	0	0.671
0.00	15	0.442	4.00	15	0.672
0.00	30	0.439	4.00	30	0.671
0.00	45	0.442			
0.00	60	0.449	8.00	0	0.690
0.00	75	0.447	8.00	15	0.690
			8.00	30	0.690
0.20	0	0.592			
0.20	15	0.591	20.00	0	0.710
0.20	30	0.591	20.00	15	0.710
			20.00	30	0.711
0.40	0	0.611			
0.40	15	0.591	40.00	0	0.740
0.40	30	0.601	40.00	15	0.741
0.40	45	0.603	40.00	30	0.743
0.40	60	0.591	40.00	45	0.749
0.40	75	0.591	40.00	60	0.750
1.00	0	0.616	80.00	0	0.771
1.00	15	0.620	80.00	15	0.781
1.00	30	0.621	80.00	30	0.782
2.00	0	0.641			
2.00	15	0.641			
2.00	30	0.651			
2.00	45	0.651			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXIII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N KNO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.449	4.00	0	0.661
0.00	15	0.447	4.00	15	0.661
0.00	30	0.446	4.00	30	0.664
0.00	45	0.446	4.00	45	0.662
0.00	60	0.446			
0.00	75	0.446	8.00	0	0.681
			8.00	15	0.681
0.20	0	0.586	8.00	35	0.683
0.20	15	0.582	8.00	50	0.683
0.20	30	0.582			
0.20	45	0.582	20.00	0	0.703
			20.00	15	0.706
0.40	0	0.603	20.00	30	0.709
0.40	25	0.607	20.00	45	0.709
0.40	40	0.606			
			40.00	0	0.726
1.00	0	0.631	40.00	15	0.730
1.00	15	0.631	40.00	30	0.731
1.00	30	0.621	40.00	55	0.732
1.00	45	0.621			
1.00	60	0.621	80.00	0	0.756
			80.00	15	0.761
2.00	0	0.641	80.00	30	0.761
2.00	15	0.641	80.00	45	0.756
2.00	30	0.641			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXIV

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.407	4.00	0	0.700
0.00	50	0.385	4.00	15	0.699
0.00	70	0.373	4.00	30	0.700
0.00	85	0.372			
0.00	100	0.370	8.00	0	0.720
0.00	115	0.370	8.00	15	0.720
0.00	130	0.369	8.00	30	0.720
0.20	0	0.622	20.00	0	0.742
0.20	15	0.621	20.00	15	0.743
0.20	30	0.621	20.00	30	0.749
			20.00	45	0.749
0.40	0	0.636			
0.40	15	0.641	40.00	0	0.770
0.40	30	0.641	40.00	15	0.771
0.40	45	0.641	40.00	30	0.772
1.00	0	0.661	80.00	0	0.810
1.00	15	0.661	80.00	15	0.802
1.00	30	0.661	80.00	30	0.805
2.00	0	0.680			
2.00	15	0.681			
2.00	40	0.681			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXV

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.407	4.00	0	0.702
0.00	15	0.402	4.00	15	0.703
0.00	30	0.397	4.00	30	0.703
0.00	45	0.391			
0.00	60	0.396	8.00	0	0.721
0.00	75	0.396	8.00	15	0.721
0.00	90	0.396	8.00	30	0.721
0.20	0	0.631	20.00	0	0.740
0.20	15	0.631	20.00	15	0.740
			20.00	30	0.741
0.40	0	0.651			
0.40	15	0.652	40.00	0	0.753
0.40	30	0.652	40.00	15	0.760
			40.00	30	0.762
1.00	0	0.670			
1.00	25	0.671	80.00	0	0.791
1.00	40	0.671	80.00	15	0.801
			80.00	30	0.811
2.00	0	0.684	80.00	45	0.811
2.00	15	0.686			
2.00	30	0.686			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXVI

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.451	4.00	0	0.685
0.00	35	0.451	4.00	20	0.686
0.00	50	0.461	4.00	35	0.686
0.00	65	0.461			
0.00	80	0.461	8.00	0	0.706
			8.00	15	0.706
0.20	0	0.611	8.00	30	0.711
0.20	15	0.609			
0.20	30	0.610	20.00	0	0.740
			20.00	15	0.742
0.40	0	0.631	20.00	30	0.742
0.40	15	0.631			
0.40	30	0.631	40.00	0	0.756
			40.00	15	0.761
1.00	0	0.650	40.00	30	0.776
1.00	15	0.651	40.00	45	0.776
1.00	30	0.651			
			80.00	0	0.806
2.00	0	0.667	80.00	15	0.826
2.00	15	0.671	80.00	30	0.830
2.00	30	0.671	80.00	45	0.831
			80.00	60	0.831

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXVII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.473	4.00	0	0.686
0.00	15	0.471	4.00	15	0.686
0.00	30	0.473	4.00	30	0.690
0.00	45	0.474	4.00	45	0.691
0.00	60	0.476			
0.00	75	0.476	8.00	0	0.702
0.00	90	0.476	8.00	15	0.710
			8.00	35	0.711
0.20	0	0.601			
0.20	15	0.602	20.00	0	0.731 ^c
0.20	30	0.601	20.00	15	0.731
			20.00	30	0.731
0.40	0	0.621			
0.40	20	0.623	40.00	0	0.742
0.40	35	0.623	40.00	20	0.749
			40.00	45	0.751
1.00	0	0.641			
1.00	15	0.643	80.00	0	0.771
1.00	30	0.646	80.00	15	0.777
1.00	45	0.646	80.00	30	0.781
			80.00	45	0.783
2.00	0	0.662	80.00	60	0.790
2.00	20	0.672	80.00	75	0.791
2.00	35	0.666			
2.00	55	0.666			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

^cFilm broke off

TABLE XXVIII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.436	8.00	0	0.681
0.00	15	0.434	8.00	15	0.681
0.00	30	0.436	8.00	30	0.681
0.00	55	0.433	8.00	45	0.681
0.00	75	0.433			
0.00	90	0.433	20.00	0	0.703
			20.00	20	0.709
0.20	0	0.579	20.00	35	0.710
0.20	15	0.576	20.00	55	0.711
0.20	30	0.576			
0.20	45	0.576	40.00	0	0.731
			40.00	15	0.736
0.40	0	0.596	40.00	30	0.740
0.40	15	0.596	40.00	45	0.741
0.40	30	0.596			
1.00	0	0.619	80.00	0	0.771
1.00	15	0.621	80.00	15	0.779
1.00	30	0.621	80.00	30	0.781
			80.00	45	0.781
2.00	0	0.641			
2.00	15	0.641	100.00	0	0.800
2.00	30	0.641	100.00	15	0.811
			100.00	30	0.814
4.00	0	0.662	100.00	45	0.821
4.00	15	0.662	100.00	60	0.826
4.00	30	0.666			
4.00	50	0.666			

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXIX

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N NH_4NO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.343	4.00	0	0.666
0.00	15	0.340	4.00	15	0.666
0.00	30	0.338	4.00	30	0.666
0.00	45	0.337			
0.00	60	0.337	8.00	0	0.683
0.00	75	0.337	8.00	15	0.686
			8.00	30	0.686
0.20	0	0.576			
0.20	15	0.576	20.00	0	0.716
0.20	30	0.576	20.00	15	0.711
			20.00	30	0.711
0.40	0	0.601			
0.40	15	0.600	40.00	0	0.731
0.40	35	0.600	40.00	15	0.731
			40.00	35	0.736
1.00	0	0.626	40.00	50	0.740
1.00	15	0.629	40.00	65	0.741
1.00	30	0.626			
1.00	45	0.626	80.00	0	0.756
			80.00	45	0.771
2.00	0	0.649	80.00	60	0.771
2.00	15	0.646			
2.00	30	0.646	100.00	0	0.786
			100.00	15	0.790
			100.00	35	0.791

^aArea of the electrode = 0.292 cm²

^bNormal hydrogen scale

TABLE XXX

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.99 N KNO_3 - 0.01 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.678	2.80	0	0.720
0.00	15	0.675	2.80	15	0.721
0.00	30	0.676	2.80	30	0.721
0.16	0	0.685	4.00	0	0.730
0.16	15	0.686	4.00	15	0.731
0.16	30	0.686	4.00	30	0.731
0.25	0	0.690	6.00	0	0.740
0.25	15	0.690	6.00	15	0.740
0.25	30	0.690	6.00	30	0.740
0.42	0	0.692	8.00	0	0.746
0.42	15	0.692	8.00	25	0.749
0.42	30	0.692	8.00	40	0.749
0.70	0	0.699	15.00	0	0.761
0.70	15	0.699	15.00	15	0.762
0.70	30	0.699	15.00	30	0.762
1.10	0	0.703	25.00	0	0.778
1.10	15	0.702	25.00	15	0.780
1.10	30	0.702	25.00	30	0.780
1.60	0	0.710			
1.60	15	0.710			
1.60	30	0.710			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXI

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.99 N KNO_3 - 0.01 AgNO_3 at 25^o C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	60	0.656	1.60	0	0.692
			1.60	15	0.692
0.16	0	0.662	1.60	30	0.692
0.16	15	0.662	1.60	60	0.692
0.16	30	0.666			
0.16	45	0.670	2.80	0	0.701
0.16	60	0.670	2.80	15	0.702
			2.80	30	0.702
0.25	0	0.671			
0.25	15	0.671	4.00	0	0.710
0.25	30	0.672	4.00	15	0.710
0.25	45	0.672	4.00	30	0.710
0.42	0	0.679	8.00	0	0.723
0.42	15	0.679	8.00	15	0.728
0.42	30	0.679	8.00	30	0.729
0.70	0	0.681	15.00	0	0.739
0.70	15	0.681	15.00	15	0.740
0.70	30	0.681	15.00	30	0.741
			15.00	45	0.741
1.10	0	0.688			
1.10	15	0.689			
1.10	30	0.689			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.99 N KNO_3 - 0.01 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.660	1.60	0	0.692
0.00	15	0.661	1.60	15	0.693
0.00	30	0.661	1.60	30	0.692
0.00	45	0.661	1.60	45	0.692
0.00	60	0.661			
			2.80	0	0.701
0.16	0	0.669	2.80	25	0.702
0.16	15	0.669	2.80	45	0.702
0.16	30	0.669			
0.16	45	0.669	4.00	0	0.710
			4.00	15	0.711
0.25	0	0.671	4.00	30	0.711
0.25	15	0.672			
0.25	30	0.672	8.00	0	0.721
			8.00	15	0.722
0.42	0	0.678	8.00	30	0.723
0.42	15	0.679	8.00	45	0.723
0.42	30	0.679			
			15.00	0	0.737
0.70	0	0.681	15.00	25	0.739
0.70	40	0.682	15.00	40	0.741
			15.00	55	0.741
1.10	0	0.689			
1.10	15	0.689			
1.10	30	0.689			
1.10	45	0.690			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXIII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.690	1.10	0	0.701
0.00	15	0.691	1.10	15	0.701
0.00	30	0.691	1.10	30	0.701
0.00	45	0.691			
			1.60	0	0.703
0.16	0	0.691	1.60	15	0.703
0.16	15	0.692	1.60	30	0.703
0.16	30	0.692			
			2.80	0	0.711
0.25	0	0.694	2.80	15	0.711
0.25	15	0.696	2.80	30	0.711
0.25	30	0.697			
0.25	45	0.697	4.00	0	0.712
			4.00	20	0.713
0.42	0	0.700	4.00	35	0.714
0.42	15	0.699	4.00	50	0.715
0.42	30	0.699	4.00	65	0.717
0.42	45	0.699	4.00	80	0.717
0.70	0	0.701	8.00	0	0.728
0.70	15	0.701	8.00	15	0.728
0.70	30	0.700	8.00	30	0.728
0.70	45	0.700			
			15.00	0	0.732
			15.00	15	0.732

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXIV

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.97 N KNO_3 - 0.03 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.686	8.00	0	0.729
0.00	15	0.688	8.00	15	0.730
0.00	30	0.690	8.00	30	0.730
0.20	0	0.691	20.00	0	0.742
0.20	15	0.691	20.00	15	0.742
0.20	30	0.691	20.00	30	0.743
0.20	45	0.691	20.00	45	0.746
			20.00	60	0.750
0.40	0	0.692	20.00	75	0.751
0.40	15	0.692	20.00	90	0.751
0.40	30	0.693	20.00	105	0.751
0.40	45	0.694			
			40.00	0	0.762
1.00	0	0.701	40.00	15	0.766
1.00	45	0.701	40.00	30	0.770
			40.00	45	0.771
2.00	0	0.708	40.00	60	0.771
2.00	15	0.708			
2.00	30	0.708	60.00	0	0.781
			60.00	35	0.791
4.00	0	0.713	60.00	60	0.720
4.00	15	0.713	60.00	75	0.772
4.00	30	0.716			
4.00	45	0.717			
4.00	60	0.717			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXV

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.90 N KNO_3 - 0.10 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.730	2.80	0	0.740
0.00	15	0.730	2.80	15	0.740
0.00	30	0.730	2.80	30	0.740
0.00	45	0.730			
			4.00	0	0.741
0.16	0	0.731	4.00	15	0.741
0.16	15	0.731	4.00	45	0.742
0.16	30	0.731	4.00	60	0.742
0.25	0	0.731	8.00	0	0.751
0.25	15	0.731	8.00	20	0.751
0.25	30	0.731	8.00	35	0.751
0.42	0	0.732	15.00	0	0.761
0.42	15	0.732	15.00	15	0.762
0.42	30	0.732	15.00	30	0.762
1.10	0	0.733	25.00	0	0.776
1.10	15	0.733	25.00	15	0.779
1.10	35	0.733	25.00	30	0.780
1.60	0	0.735			
1.60	15	0.736			
1.60	30	0.736			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXVI

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.90 N KNO_3 - 0.10 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.726	1.60	0	0.732
0.00	15	0.724	1.60	55	0.732
0.00	30	0.724			
0.00	45	0.724	2.80	0	0.736
			2.80	15	0.737
0.16	0	0.730	2.80	30	0.739
0.16	15	0.730	2.80	45	0.739
0.16	30	0.730			
			4.00	0	0.741
0.25	0	0.730	4.00	15	0.741
0.25	15	0.730	4.00	30	0.741
0.25	30	0.730			
			8.00	0	0.749
0.42	0	0.731	8.00	15	0.749
0.42	15	0.731	8.00	30	0.750
0.42	30	0.731	8.00	45	0.750
0.70	0	0.731	15.00	0	0.759
0.70	15	0.731	15.00	15	0.761
0.70	30	0.731	15.00	30	0.762
			15.00	45	0.762
1.10	0	0.731			
1.10	15	0.731	25.00	0	0.773
1.10	30	0.731	25.00	15	0.780
			25.00	30	0.780

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXVII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.70 N KNO_3 - 0.30 N AgNO_3 at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.744	8.00	0	0.760
0.00	15	0.746	8.00	25	0.760
0.00	30	0.746	8.00	40	0.760
0.00	45	0.746			
0.00	50	0.746	20.00	0	0.761
			20.00	20	0.762
0.20	0	0.750	20.00	45	0.762
0.20	15	0.750			
0.20	30	0.750	40.00	0	0.769
			40.00	15	0.770
0.40	0	0.750	40.00	30	0.771
0.40	15	0.751	40.00	45	0.771
0.40	30	0.751			
0.40	50	0.751	60.00	0	0.775
			60.00	15	0.780
1.00	0	0.752	60.00	30	0.781
1.00	25	0.751	60.00	45	0.781
1.00	40	0.751			
1.00	55	0.752	100.00	0	0.789
1.00	70	0.752	100.00	15	0.790
			100.00	30	0.791
2.00	0	0.753	100.00	45	0.791
2.00	15	0.753	100.00	60	0.792
2.00	55	0.753			
4.00	0	0.756			
4.00	40	0.758			
4.00	55	0.758			

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

TABLE XXXVIII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.70 N KNO_3 - 0.30 N AgNO_3 at 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.740	4.00	0	0.747
0.00	15	0.739	4.00	15	0.747
0.00	30	0.739	4.00	40	0.747
0.00	45	0.739			
0.00	60	0.739	8.00	0	0.750
			8.00	15	0.750
0.20	0	0.741	8.00	20	0.750
0.20	15	0.741			
0.20	30	0.741	20.00	0	0.756
			20.00	15	0.758
0.40	0	0.741	20.00	45	0.760
0.40	15	0.741			
0.40	30	0.741	40.00	0	0.770
			40.00	15	0.771
1.00	0	0.742	40.00	30	0.773
1.00	15	0.743			
1.00	30	0.743	80.00	0	0.796
			80.00	15	0.809
2.00	0	0.744	80.00	30	0.790
2.00	15	0.744	80.00	45	0.793
2.00	30	0.744	80.00	50	0.800

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

TABLE XXXIX

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.70 N NH_4NO_3 - 0.30 N AgNO_3 at 25° C

$I \times 10^3$, (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.749	8.00	0	0.760
0.00	40	0.749	8.00	15	0.760
0.00	55	0.749	8.00	30	0.760
0.20	0	0.751	20.00	0	0.764
0.20	15	0.751	20.00	15	0.768
0.20	30	0.751	20.00	30	0.769
			20.00	45	0.769
0.40	0	0.751			
0.40	15	0.751	40.00	0	0.781
0.40	30	0.751	40.00	15	0.781
			40.00	30	0.783
1.00	0	0.751	40.00	45	0.789
1.00	15	0.751	40.00	60	0.789
1.00	30	0.751			
			80.00	0	0.811
2.00	0	0.752	80.00	15	0.816
2.00	15	0.752	80.00	30	0.821
2.00	30	0.752	80.00	45	0.829
			80.00	60	0.832
4.00	0	0.753	80.00	75	0.839
4.00	15	0.753			
4.00	30	0.753			

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

TABLE XL

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.70 N NH_4NO_3 - 0.30 N AgNO_3 at 25° C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.746	4.00	0	0.752
0.00	15	0.745	4.00	15	0.752
0.00	30	0.744	4.00	30	0.752
0.00	45	0.744			
0.00	60	0.744	8.00	0	0.758
			8.00	15	0.758
0.20	0	0.749	8.00	30	0.759
0.20	15	0.749			
0.20	30	0.749	20.00	0	0.763
			20.00	25	0.764
0.40	0	0.749	20.00	40	0.767
0.40	15	0.749	20.00	70	0.770
0.40	30	0.749	20.00	85	0.770
1.00	0	0.750	40.00	0	0.781
1.00	15	0.750	40.00	25	0.781
1.00	30	0.750	40.00	45	0.781
2.00	0	0.751	80.00	0	0.801
2.00	15	0.751	80.00	15	0.809
2.00	30	0.751	80.00	40	0.823
			80.00	55	0.830

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

TABLE XLI

Time Behavior of the Dissolution Potential of the
Silver Electrode in 0.70 N NH_4NO_3 - 0.30 N AgNO_3 at 50° C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.741	4.00	0	0.744
0.00	15	0.739	4.00	15	0.744
0.00	30	0.740	4.00	30	0.744
0.00	45	0.739			
0.00	60	0.739	8.00	0	0.749
			8.00	15	0.749
0.20	0	0.741	8.00	30	0.753
0.20	15	0.741			
0.20	30	0.741	20.00	0	0.752
			20.00	15	0.753
0.40	0	0.741	20.00	30	0.753
0.40	15	0.741			
0.40	30	0.741	40.00	0	0.763
			40.00	15	0.769
1.00	0	0.742	40.00	30	0.769
1.00	15	0.742			
1.00	30	0.742	80.00	0	0.789
			80.00	15	0.790
2.00	0	0.742	80.00	30	0.792
2.00	25	0.743	80.00	45	0.798
2.00	40	0.743	80.00	60	0.800

^aArea of the electrode = 0.282 cm²

^bNormal hydrogen scale

TABLE XLII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N AgNO₃ at 25° C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.782	1.10	0	0.791
0.00	15	0.782	1.10	15	0.791
0.00	35	0.781	1.10	30	0.791
0.00	50	0.781			
			1.60	0	0.791
0.16	0	0.788	1.60	15	0.791
0.16	15	0.789			
0.16	30	0.789	4.00	0	0.792
0.16	45	0.789	4.00	15	0.792
			4.00	30	0.792
0.25	0	0.790			
0.25	15	0.790	8.00	0	0.799
0.25	30	0.790	8.00	15	0.799
			8.00	30	0.799
0.42	0	0.790			
0.42	35	0.790	20.00	0	0.806
0.42	50	0.790	20.00	15	0.807
			20.00	30	0.809
0.70	0	0.791	20.00	45	0.809
0.70	25	0.791			
0.70	40	0.791			

^aArea of the electrode = 0.723 cm²

^bNormal hydrogen scale

TABLE XLIII

Time Behavior of the Dissolution Potential of the
Silver Electrode in 1.00 N AgNO₃ at 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
0.00	0	0.796	1.10	0	0.801
0.00	15	0.794	1.10	30	0.801
0.00	30	0.791	1.10	45	0.801
0.00	45	0.791			
			1.60	0	0.802
0.16	0	0.799	1.60	15	0.802
0.16	15	0.799	1.60	30	0.802
0.16	30	0.799			
			4.00	0	0.803
0.25	0	0.800	4.00	15	0.811
0.25	15	0.800	4.00	30	0.811
0.25	30	0.800			
			8.00	0	0.820
0.42	0	0.800	8.00	15	0.820
0.42	15	0.801	8.00	30	0.820
0.42	30	0.801			
			15.00	0	0.831
0.70	0	0.801	15.00	15	0.831
0.70	15	0.801	15.00	30	0.831
0.70	30	0.801			
			20.00	0	0.840
			20.00	15	0.841
			20.00	30	0.841

^aArea of the electrode = 0.664 cm²

^bNormal hydrogen scale

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IX. VITA

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