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THE ANODIC DISSOLUTION OF MOLYBDENUM IN ACID SULFATE SOLUTIONS

BY

CHING-KUO CHEN, 1941

A 440

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI - ROLLA

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1969

T2213
75P
91

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. W. Johnson, Professor of Chemical Engineering, who served as research advisor, and Dr. W. J. James, Professor of Chemistry and Director of the Graduate Center for Materials Research. Their help, guidance, and encouragement are sincerely appreciated.

Thanks are extended to the Graduate Center for Materials Research, University of Missouri - Rolla, for the use of its equipment and for a research scholarship.

The author is deeply indebted to his parents for their support and encouragement which enabled him to pursue advanced studies in the United States.

ABSTRACT

The apparent valence of molybdenum during anodic dissolution was determined in 1.0 N H_2SO_4 (pH = 0.38), and $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ (pH = 1.50 and 3.38) with and without Cl^- ion additions. The current density was varied from 0.001 to 0.1 $\text{amp}\cdot\text{cm}^{-2}$. The results lead to the following conclusions:

1. The apparent valence in all solutions is approximately +6, independent of current density and pH.
2. Chloride ions have no effect on the apparent valence.
3. X-ray analyses of the surface films formed on the anode showed them to be highly amorphous with a probable composition of $\text{MoO}_{2.65}$ - $\text{MoO}_{2.89}$.

Potential-current density relationships were also obtained in the electrolytes mentioned above. At potentials in the region slightly more positive than the rest potential, linear Tafel sections with slopes of about 0.060 v were found. The proposed dissolution mechanism is

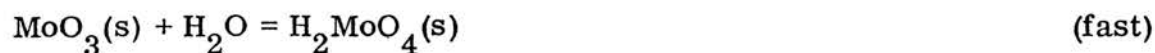
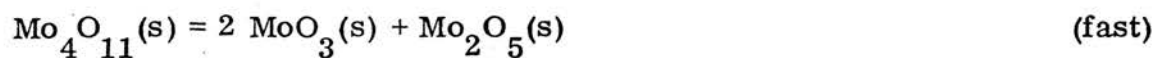
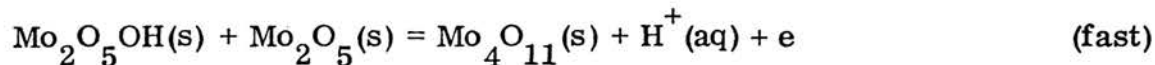
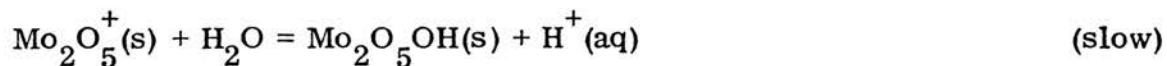


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I. INTRODUCTION

The world's resources of metals are decreasing. Due to this and the cost of replacing corroded materials, it has come to be realized that prevention is better than cure. The increasing demand for molybdenum and molybdenum alloys has stimulated a great amount of research into the corrosion characteristics of these materials. The result of such research has assisted in the development of suitable molybdenum alloys and protective coatings to retard corrosion.

When a molybdenum anode and a suitable cathode are immersed in an oxygen-free electrolyte and are connected to a direct current power source, molybdenum is dissolved. This process is called anodic dissolution and a study of it is useful for many reasons:

1. The apparent valence of the metal undergoing dissolution can be determined.
2. An empirical expression for the dissolution rate can be established.
3. A dissolution reaction mechanism can be hypothesized that may aid in retarding corrosion and predicting behavior in other environments.

The mechanism of the anodic dissolution of molybdenum has been formulated only in very vague terms. The purpose of this investigation was to study the dissolution in sulfuric acid solutions of various pH and if possible to establish a mechanism consistent with the data. Toward this end, experiments were performed to determine the relationships between the current density, potential, pH, and faradaic efficiency during dissolution. The effect of chloride ion on the process was also determined.

II. LITERATURE REVIEW

The chemistry of molybdenum is among the most complex of the transition elements. It is classed in group VI and has a wide variety of stereochemistries in addition to a variety of oxidation states.

Molybdenum is only slowly oxidized in the atmosphere at ordinary temperature and retains its metallic lustre almost indefinitely. (1) Jones and co-workers (2) found that the oxidation-scale on molybdenum consisted of two or three oxide layers whose composition depended upon temperature and time. The outermost layer was the volatile MoO_3 and the inner layers had compositions very close to MoO_2 but did not exhibit x-ray patterns corresponding to MoO_2 . The rate of vaporization of MoO_3 and the mechanism of molybdenum oxidation were determined. The weight change was initially parabolic but later became linear with time. This was attributed to a non-protective outer layer that thickened and retarded the rate of oxygen diffusion.

There are also oxides referred to as "molybdenum blues". (1) Their compositions are not exact, varying from $\text{MoO}_{2.5}$ to MoO_3 . The oxidation state of molybdenum, between V and VI, is probably due to ions in both states occupying sites in an oxygen-defective MoO_3 lattice.

Besson and Drautzburg (3) studied the anodic dissolution of molybdenum in 1 N H_2SO_4 and found it to proceed practically quantitatively to the +6 oxidation state. They also studied the polarization of molybdenum in aqueous solutions and found the polarization curves to be continuous up to the highest current densities attained (about $100 \text{ ma} \cdot \text{cm}^{-2}$). Semilogarithmic plots of potential vs. current

density were linear. The slopes of the curves were independent of the electrolyte pH but their position was shifted on the potential scale. They concluded that molybdenum is highly polarizable as a result of the abnormally small transfer coefficient (0.1-0.2), the magnitude of which depended on the pH of the medium and the adsorption of anions on the metal surface.

Lavrenko and Pen'kov (4) studied the anodic oxidation in saturated boric acid solutions at a current density of about $50 \text{ ma} \cdot \text{cm}^{-2}$ (potentials up to 200 v). They found a thick many-layered oxide film containing MoO_2 and MoO_3 to be formed on the electrode surface.

Pozdeeva and co-workers (5) have reported polarization curves for molybdenum in $1.0 \text{ N H}_2\text{SO}_4$. They found dissolution to begin at approximately 0.40-0.45 v (SHE) and to increase exponentially with increasing potential. Upon passage of current, the electrode darkened and became covered with an oxide film which was not protective. Molybdenic acid, H_2MoO_4 , was said to have passed into solution. At 0.74 v, the curve had a characteristic bend after which a limiting current was reached. A different oxide, the γ -phase (see Table I) was formed on the surface at about 0.75-0.80 v. It has a higher electrical resistance than the lower oxides and at potentials greater than 0.76 v can be electrochemically converted to MoO_3 . At potentials greater than 0.8 v, a black phase began to separate from the electrode. This process was accompanied by the formation of a still different surface layer consisting of the β , β' , and α phases. The compositions and properties of the oxides for the Mo-O system are shown in Table I.

TABLE I. COMPOSITIONS AND PROPERTIES OF THE
OXIDE PHASES IN THE SYSTEM Mo-O

Phase	Composition and Region		Specific
	of Homogeneity		Resistance (Ω cm)
δ	$\text{MoO}_{1.97}$ - $\text{MoO}_{2.08}$		<0.1
γ	$\text{MoO}_{2.65}$ - $\text{MoO}_{2.75}$		0.95-1.5
β	$\text{MoO}_{2.87}$		3840
β'	$\text{MoO}_{2.89}$		3.95
α	MoO_3		$>10^7$

The formation, oxidation, chemical solution, and scaling of the multi-layered film determines the anodic behavior of molybdenum at potentials greater than 0.75 v. At potentials greater than 1.0 v, the rate of oxidation of the phases is independent of potential. No oxygen was evolved at potentials up to 3.5 v.

Hampel (7) and Deltombe, De Zoubov, and Pourbaix (8) found molybdenum to have good resistance to non-oxidizing acids and to be only slightly attacked by hydrofluoric acid. It was attacked appreciably by dilute nitric acid acting as an oxidizing agent. An oxide layer, MoO_3 , which protects the metal from further attack is formed in concentrated nitric acid.

Heuman and Hauck (11) studied the anodic dissolution of molybdenum and indicated that the mechanism of molybdate formation in the pH range 0-14 does not alter and is independent of anions except for OH^- . The black surface layer was found to be amorphous and highly porous and its thickness increased linearly with time. It was thought to consist mainly of MoO_2 .

The fact that molybdenum does not dissolve appreciably in many non-oxidizing acids is probably partially due to its high hydrogen overpotential. In hydrochloric acid, a film of insoluble chloride is formed which passivates the metal. The pretreatment is also important as it can render the metal either active or passive. Chemical passivators include oxidizing agents such as nitric acid, concentrated chromic acid, and ferric chloride, as well as the non-oxidizing acids, dilute hydrochloric and sulphuric.

Few comprehensive studies have been reported on the polarization of molybdenum. Some reports (6-10) have shown that it is active in acid solutions

at potentials of 0.2-0.5 v and passes into solution in the form of MoO_4^{-2} ions.

The potential region for which molybdenum is passive is not known. Pourbaix (8) has predicted that the metal will dissolve as Mo^{+3} in acids at low anodic potentials.

III. EXPERIMENTAL

The purpose of this investigation was to study the anodic dissolution of molybdenum in sulfate solutions ($\text{pH} = 0.38 - 3.38$). Above a pH of 3.3, these solutions have very little buffering capacity and large changes in pH can occur during the course of a run. The effects of Cl^- additions were also of interest as they tend to promote corrosion with many passive metals.

The experimental plan consisted of the following major phases: (1) the effect of electrolyte and current density on the apparent valence of molybdenum undergoing anodic dissolution, and (2) polarization behavior of molybdenum during anodic dissolutions. All studies were made at 25°C .

A. Materials.

The list of materials is given in Appendix A.

B. Equipment.

The list of equipment is presented in Appendix B.

C. The Apparent Valence of Molybdenum Undergoing Anodic Dissolution.

1. Apparatus. The apparatus consisted of an electrolysis cell with separated compartments of 400 milliliter capacity. The molybdenum anode, a platinized-platinum cathode, a milliammeter, a decade power resistor, and a knife-blade switch were all connected in series with a d. c. power supply. A diagram of the apparatus is shown in Figure 1. A timer with one-second divisions was used for measuring the elapsed time. The cell was partially immersed in a water-bath controlled at $25 \pm 0.1^\circ\text{C}$.

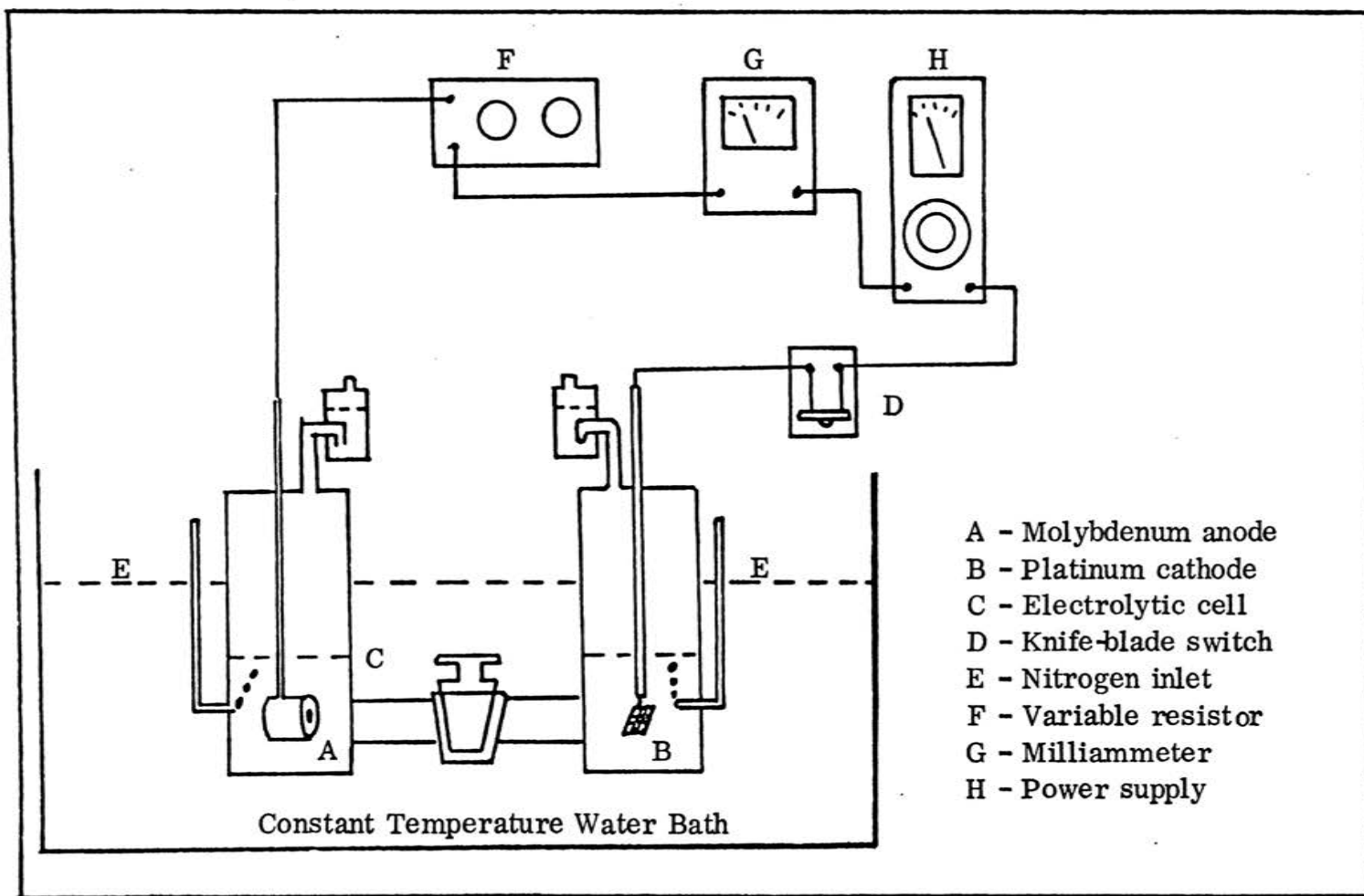


Figure 1. Diagram of the apparatus used for the measurement of the apparent valence of molybdenum undergoing anodic dissolution.

2. Procedure. Approximately 250 millimeters of electrolyte were transferred into the electrolytic cell and the cell placed in the constant temperature bath. A nitrogen purge of the electrolyte and cell was begun and the system allowed to come to constant temperature. The molybdenum specimen for the anode was cut from a cylindrical metal bar of 99.9 percent purity. The anode surface was smoothed with a belt grinder until free of visible defects and then polished on a hand grinder with 240, 320, 400, and 600 abrasive grit papers. Finally, the specimen was etched in dilute nitric acid for several minutes to produce a smooth clear surface, rinsed with distilled water, placed in a desiccator to dry, and weighed. It was then mounted in a teflon holder (see Figure 2) and together with a platinum cathode put into the appropriate compartments of the cell and connected into the external circuit (see Figure 1).

To begin an experiment, the knife-blade switch was closed and the current kept at a steady value by means of the variable resistance box. The timer and milliammeter were used to determine the number of coulombs passed. At the end of a test run, the molybdenum electrode was taken out, rinsed, dried, and reweighed to determine the weight of molybdenum dissolved. The same procedure was employed for all electrolysis experiments.

3. Data and Results. The data from this part of the experimentation are given in Appendix C. A brief summary of the results for each solution follows:

a. 1.0 N H₂SO₄ (pH = 0.38). The anodic dissolution of molybdenum was observed in 1.0 N H₂SO₄ at current densities which varied from 0.001 to 0.1 amp·cm⁻². The data are shown in Table III, Appendix C. The apparent

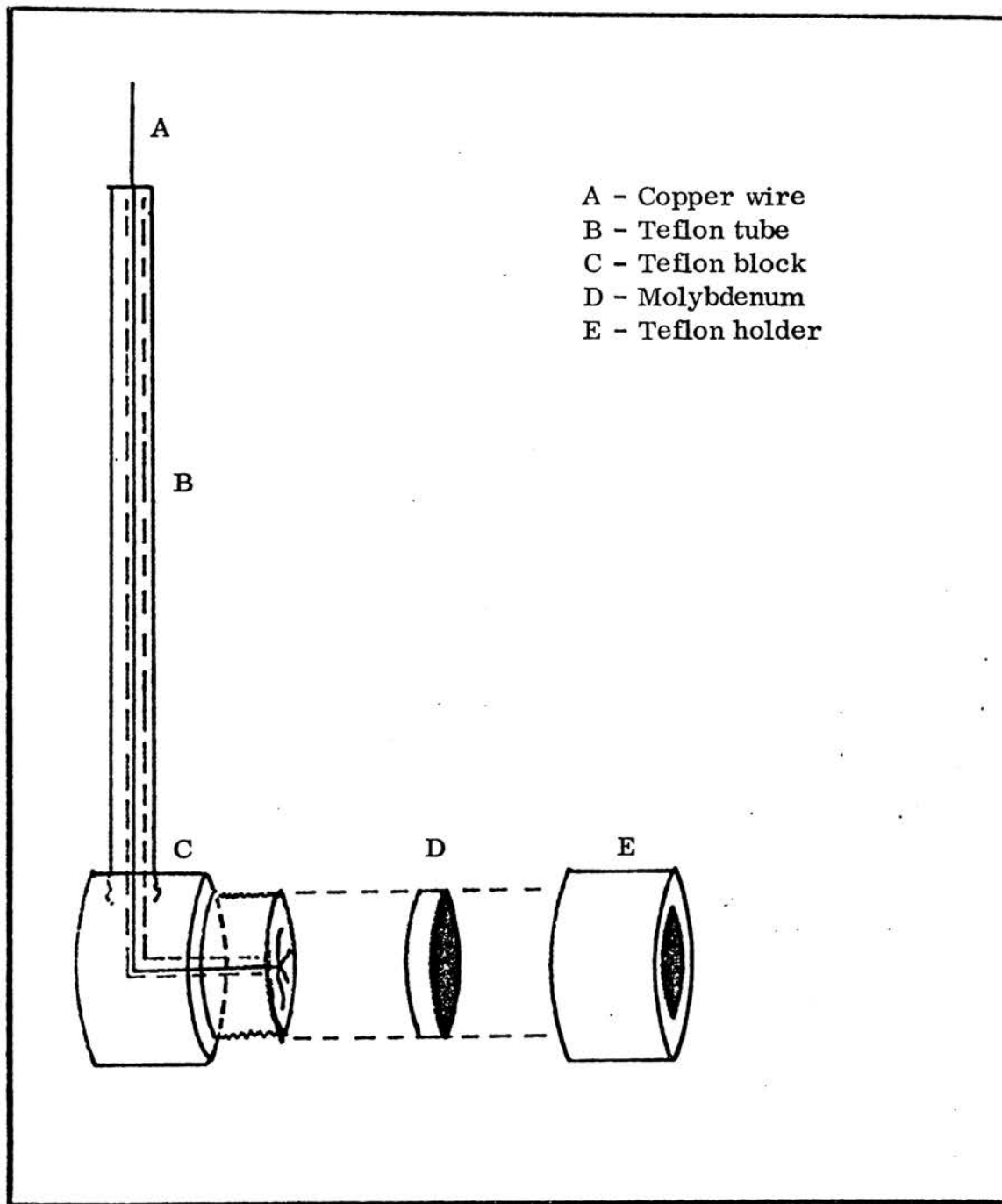


Figure 2. Diagram of the teflon holder used for the apparent valence measurements.

valences were approximately six at all current densities. During the electrolysis, a dark blue film was formed on the molybdenum surface. Measurements were also made with KCl additions in which the Cl^- concentration was varied from 0.001 to 0.1 N. These data are shown in Tables IV and V, Appendix C. It can be seen that the apparent valence was not affected by the Cl^- . Also, no changes were noted in the film formed on the molybdenum surface.

b. 0.1 N H_2SO_4 (pH = 1.38). The anodic dissolution of molybdenum in 0.1 N H_2SO_4 -KCl was carried out at current densities ranging from 0.001 to 0.1 amp·cm⁻² and Cl^- ion concentrations varying from 0.001 to 0.1 N. The data are shown in Tables VI and VII, Appendix C. The apparent valences were approximately +6 in 0.1 N H_2SO_4 -0.1 N KCl. Small negative deviations were noted in solutions with decreased Cl^- concentration, especially at higher current densities. During the electrolysis, the previously observed dark blue film was formed on the anode surface. It was loosely held and could be removed by rinsing with a stream of distilled water. The metal surface beneath the film was smooth and shiny at low current densities but was smooth and dull at high.

c. H_2SO_4 - K_2SO_4 solutions (pH = 1.50 and 3.38). The dissolution in H_2SO_4 - K_2SO_4 solutions was carried out at current densities ranging from 0.001 to 0.1 amp·cm⁻². The solutions contained the amounts of H_2SO_4 and K_2SO_4 to give the desired pH with a unit ionic strength.

The apparent valences were again approximately +6 with the dark blue film formed on the electrode surface. The data are shown in Tables VIII and IX, Appendix C. At all current densities, small portions of the film were continually

spalled off the surface. Chloride additions were also made to these solutions in which the Cl^- concentration varied from 0.001 to 0.1 N and the current density from 0.003 to 0.3 amp·cm⁻². These data are shown in Tables X to XIII, Appendix C. The +6 valence and the dark blue film were again found.

4. Sample Calculations. The data from the experiment in 1.0 N H_2SO_4 (Table III) have been used to illustrate the calculations. The same method was used to calculate the apparent valence in all the solutions.

According to Faraday's law, the weight of molybdenum dissolved assuming a valence of +6 is:

$$W_a = \frac{I t A}{n F}$$

$$= \frac{(0.0283) (9,000) (95.95)}{(6) (96,486)} = 0.0422 \text{ gm.}$$

The apparent valence can be calculated by the equation:

$$V_i = \frac{(W_a)(n)}{(W_e)}$$

$$= \frac{(0.0422) (6)}{(0.0424)} = 5.97$$

Where, W_a = calculated weight-loss of molybdenum, grams

I = current, amperes

t = time of run, seconds

A = atomic weight of molybdenum = 95.95

n = normal valence of molybdenum = +6

F = Faraday's constant = 96,486 amp·sec/gm-equiv

W_e = experimental weight-loss of molybdenum, grams

V_i = apparent valence

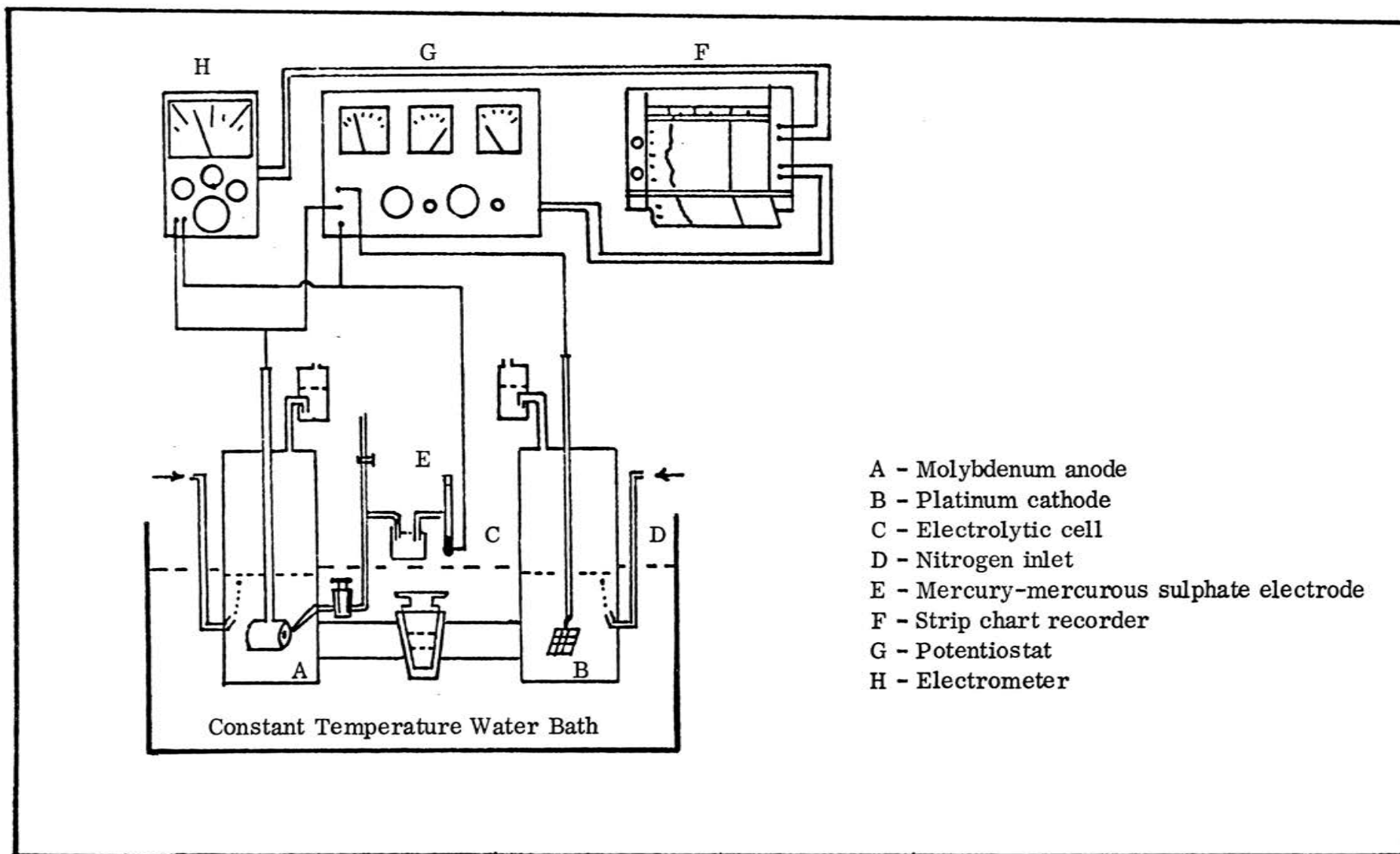


Figure 3. Diagram of the apparatus used for the measurement of the anodic current-potential relationship of molybdenum at 25°C.

D. The Relationship Between Current Density and Potential for the Dissolution of Molybdenum.

1. Apparatus. A diagram of the apparatus for this portion of the investigation is shown in Figure 3. The temperature was controlled at $25 \pm 0.1^{\circ}\text{C}$. A mercury-mercurous sulphate ($1.0\text{ N H}_2\text{SO}_4$) reference electrode, standard potential = 0.652 volts (12), was connected to the anode through a Luggin capillary and a salt bridge. A high impedance electrometer was used to measure the potential difference between the anode and reference electrode. During polarization, the difference was maintained at arbitrary constant values with a potentiostat.

2. Procedure. The electrode preparation and the initial portion of the experimental runs were the same as for the apparent valence studies. When the anode had reached a steady potential without current flowing (rest potential), a predetermined potential (more positive than the rest potential) was impressed on the anode with the potentiostat. The constant potential operation was continued until the current became relatively steady (<10% change per hour). The potential was then increased to a higher value and this sequence repeated until the desired potential region was covered. A diagram of the teflon holder for this portion of the work is shown in Figure 4.

3. Data and Results. The anodic dissolution studies were made in the same electrolytes as the apparent valence studies. All potentials are referred to the standard hydrogen electrode (SHE) at 25°C . A summary of the experimental results follows.

a. 1.0 N H₂SO₄ (pH = 0.38). The results of these studies with and without Cl⁻ additions are shown in Tables XIV to XVI. The rest potentials of the molybdenum electrode varied from 0.342 to 0.352 v. The linear portions of the Tafel curves in the potential region 0.392 to 0.450 v had slopes of about 0.060 v.

For potentiostatic operation, the highest potential that could be attained was about 0.65 volts. A galvanostatic technique using a high voltage power supply was used to polarize the molybdenum anode to higher potentials. These results are shown in Figure 5 and Table XXV, Appendix D. No gas evolution was observed.

Under constant current conditions, the surface film on the anode appeared to thicken and was accompanied by a continual increase in the anode potential. At a current density of about 20 ma·cm⁻², the film spalled off the electrode surface. At a current density of 260 ma·cm⁻², the potential never assumed a steady value, but continually cycled between 0.45 and 95 v. A deep blue color was formed in the electrolyte at current densities above 200 ma·cm⁻². No gas evolution was observed.

b. 0.1 N H₂SO₄-KCl (pH = 1.38). These data are shown in Tables XVII and XVIII, Appendix D. Polarization curves are shown in Figure 7. The rest potential in these electrolytes varied from 0.344 to 0.349 v. There was no noticeable effect of Cl⁻ on the polarization behavior. The linear Tafel region was approximately contained within 0.35 to 0.45 v. The slopes were 55 to 61 mv. No gas evolution was observed.

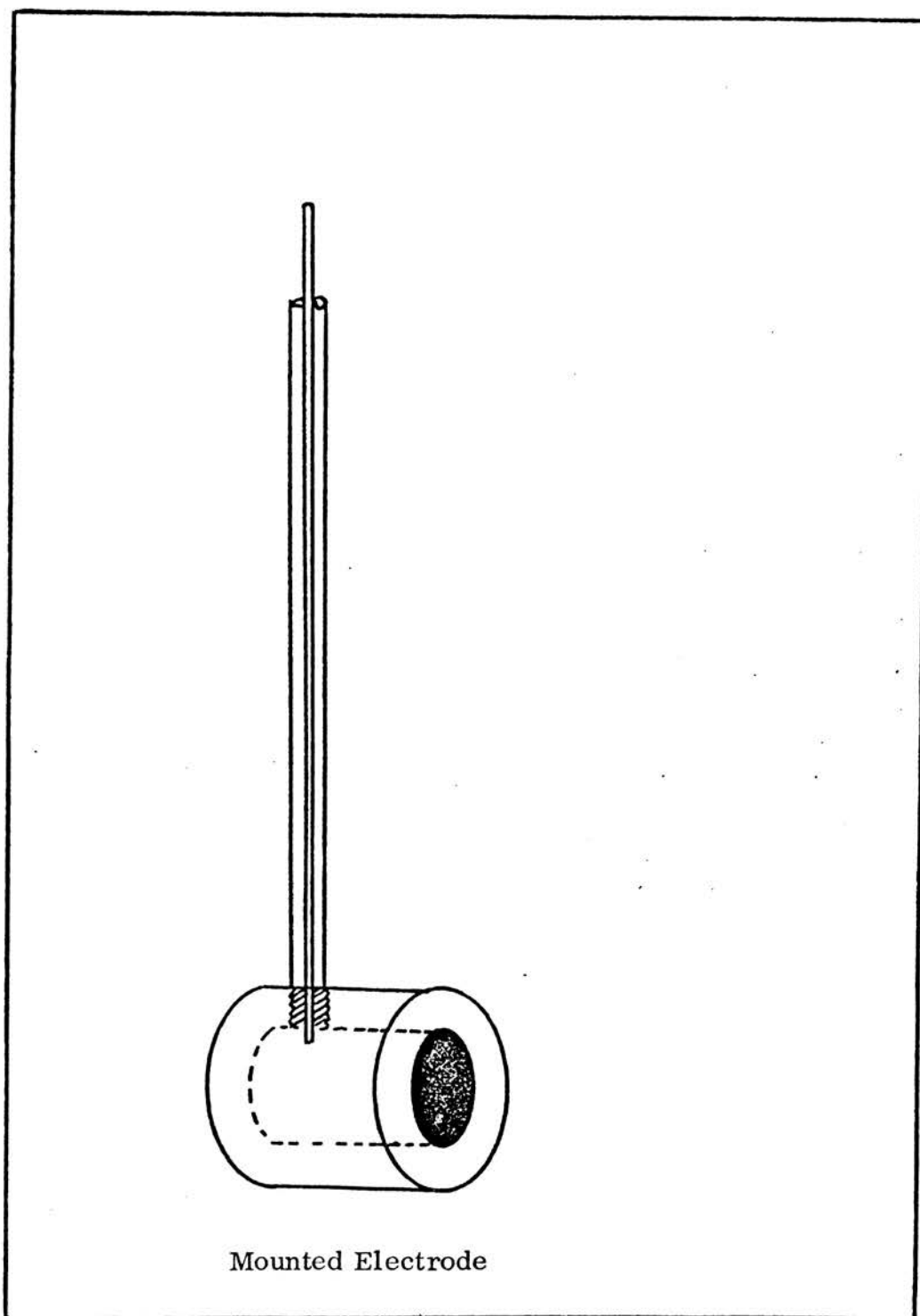


Figure 4. Diagram of the molybdenum electrode used for current-potential measurements at 25^oC.

c. $\underline{\text{H}_2\text{SO}_4 - \text{K}_2\text{SO}_4}$ (pH = 1.50). The results of the studies in these solutions are shown in Tables XIX to XXI, Appendix D. Tafel plots are shown in Figure 8. The rest potentials varied from 0.307 to 0.327 v. Limiting currents were reached in these solutions. No gas evolution was observed.

d. $\underline{\text{H}_2\text{SO}_4 - \text{K}_2\text{SO}_4}$ (pH = 3.38). These data are shown in Tables XXII to XXIV, Appendix D. Potential-current density plots are shown in Figure 9. A small region of passivation was found for Cl^- ion concentrations of 0.001 and 0.1 N. The rest potentials in these electrolytes were in the region of 0.282 to 0.300 v. The linear Tafel region was again between 0.35 to 0.45 v. No gas evolution was observed.

4. Sample Calculations. The method for calculating the potential is illustrated below.

$$E = E_r - E_m$$

E = potential (standard hydrogen scale).

E_r = Potential of mercury-mercurous sulphate (1.0 N H_2SO_4)
reference electrode.

E_m = potential read from the electrometer.

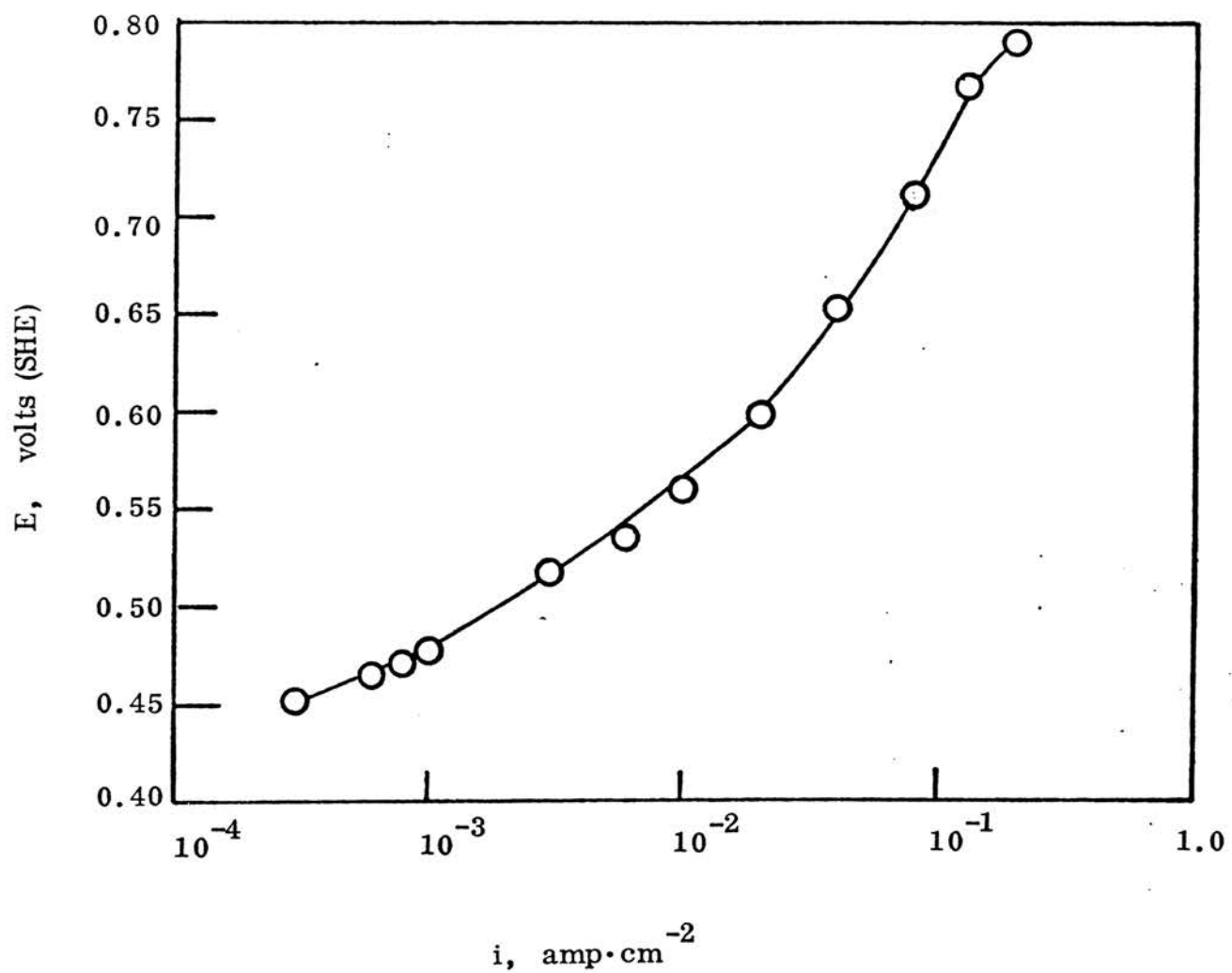


Figure 5. Current-potential relationship for the anodic dissolution of molybdenum in 1.0 N H₂SO₄ (pH = 0.38) at 25^oC by the galvanostatic technique.

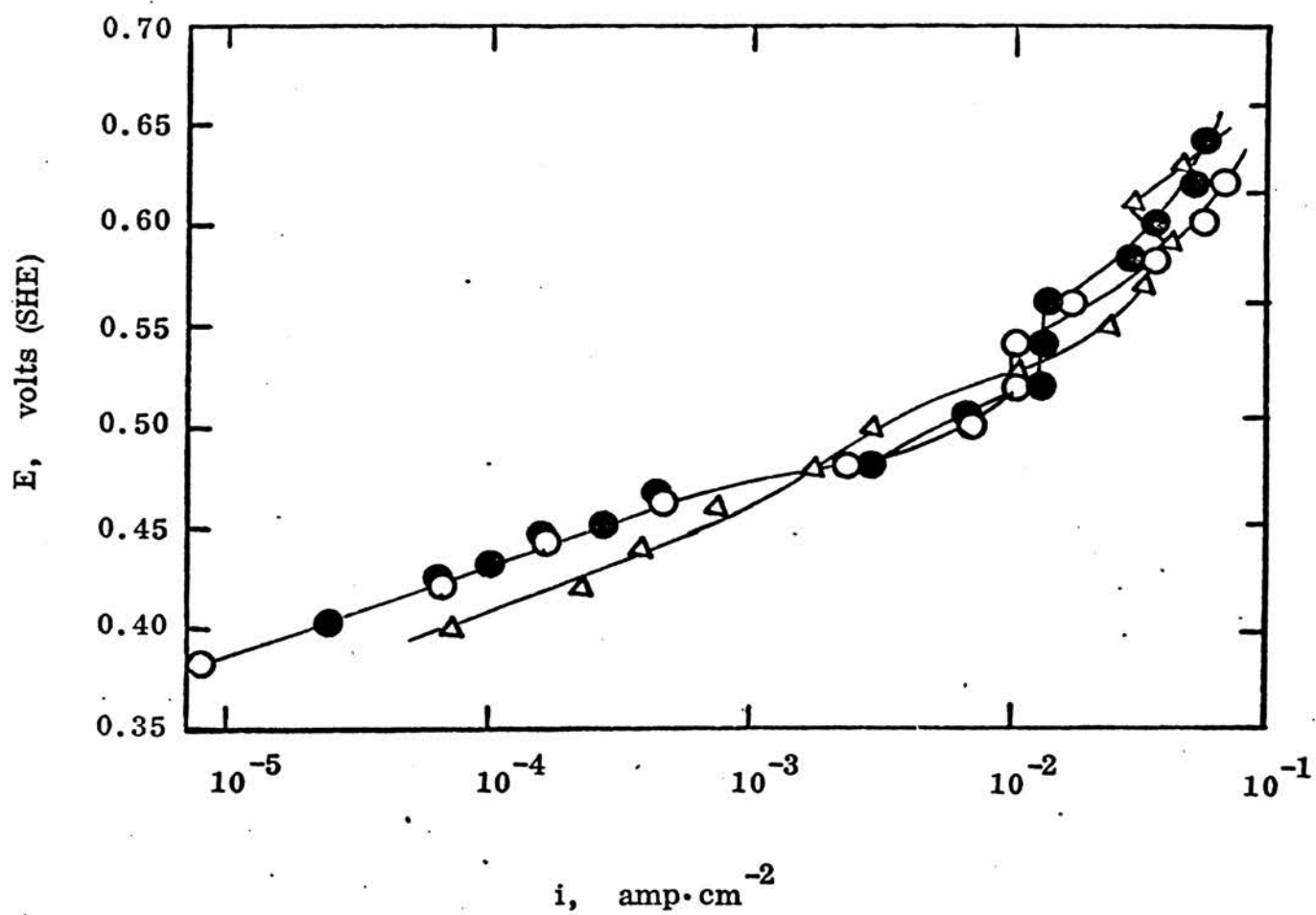


Figure 6. Tafel curves for the anodic dissolution of molybdenum in 1.0 N H₂SO₄ (pH = 0.38) at 25°C. (○, 1.0 N H₂SO₄; ●, 1.0 N H₂SO₄ - 0.001 N KCl; △, 1.0 N H₂SO₄ - 0.1 N KCl)

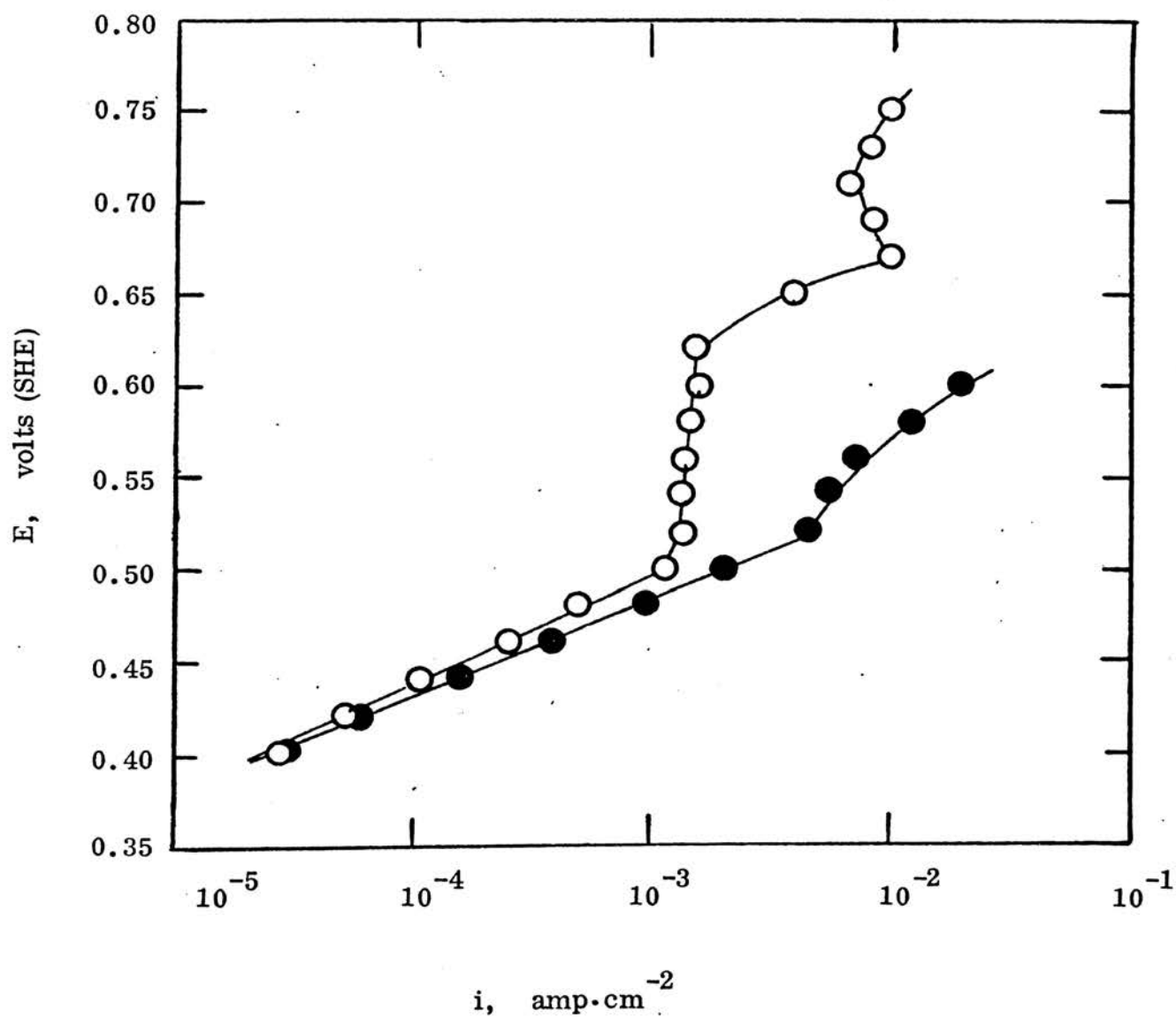


Figure 7. Tafel curves for the anodic dissolution of molybdenum in 0.1 N H_2SO_4 (pH = 1.38) at 25^o C. (●, 0.1 N H_2SO_4 - 0.001 N KCl; ○, 0.1 N H_2SO_4 - 0.1 N KCl)

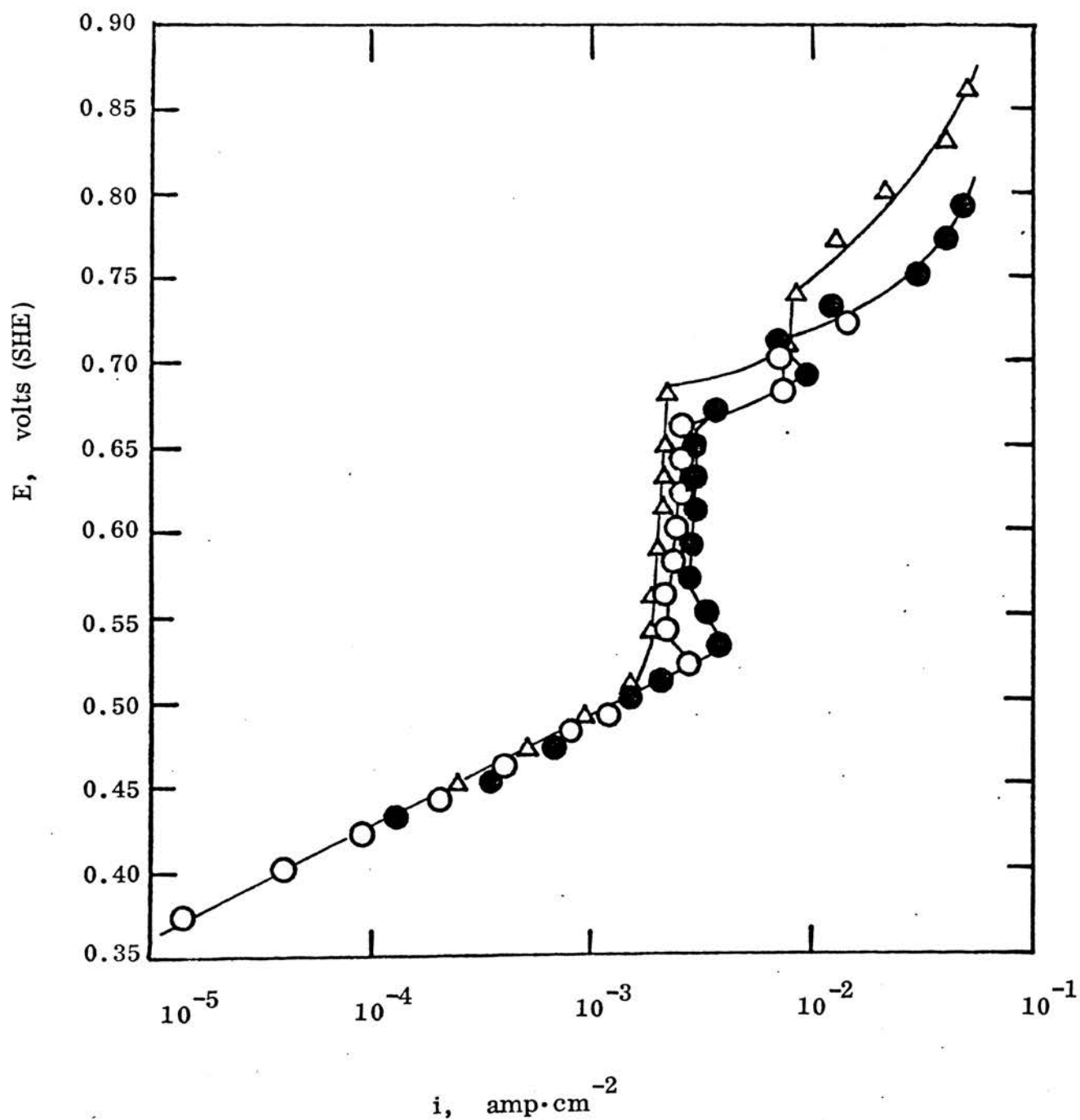


Figure 8. Tafel curves for the anodic dissolution of molybdenum in $0.240 \text{ N H}_2\text{SO}_4 - 0.760 \text{ N K}_2\text{SO}_4$ solutions ($\text{pH} = 1.50$) at 25°C . (\circ , $0.240 \text{ N H}_2\text{SO}_4 - 0.760 \text{ N K}_2\text{SO}_4$; Δ , $0.240 \text{ N H}_2\text{SO}_4 - 0.760 \text{ N K}_2\text{SO}_4 - 0.001 \text{ N KCl}$; \bullet , $0.240 \text{ N H}_2\text{SO}_4 - 0.760 \text{ N K}_2\text{SO}_4 - 0.1 \text{ N KCl}$)

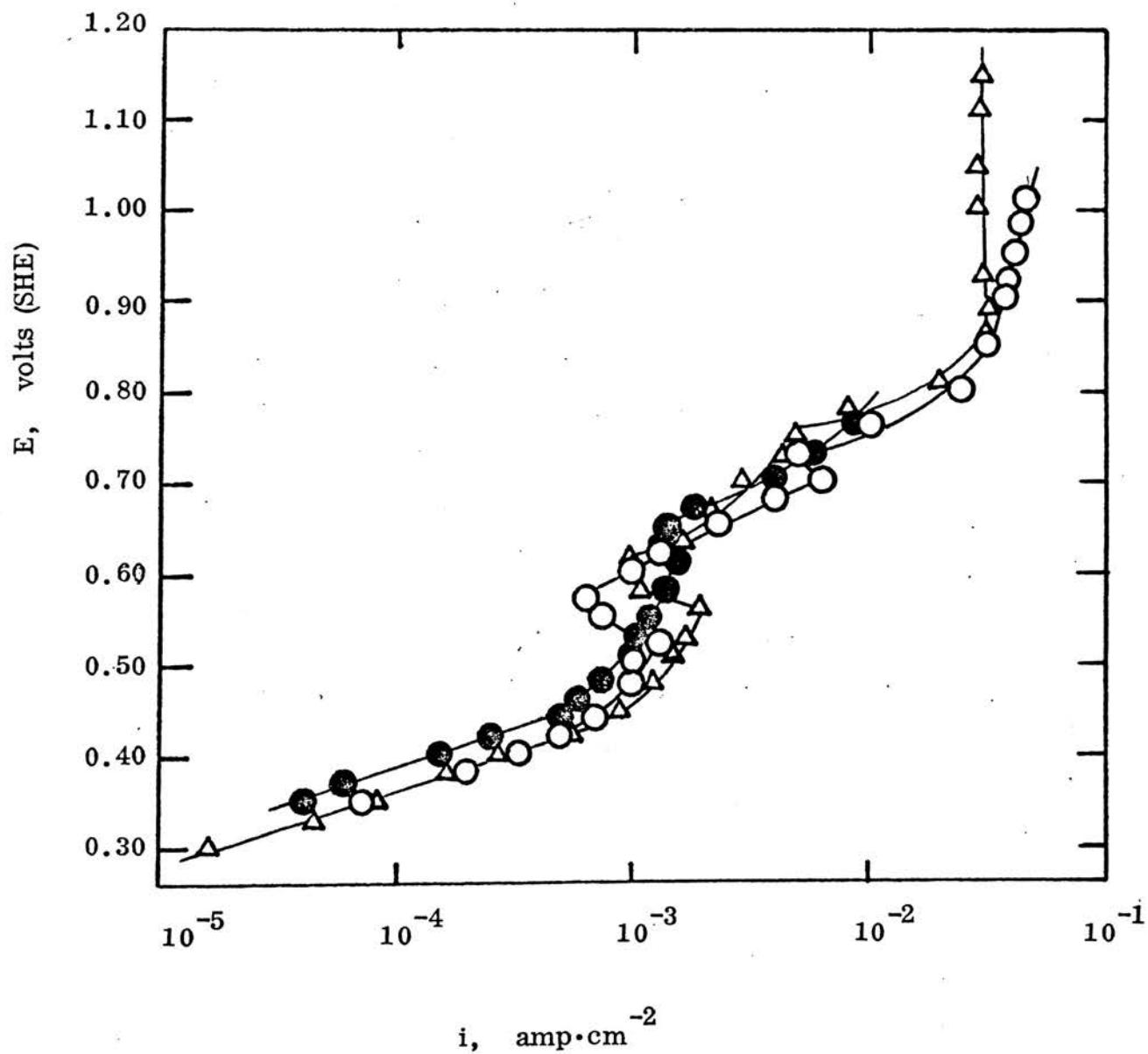


Figure 9. Tafel curves for the anodic dissolution of molybdenum in $0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4$ solutions ($\text{pH} = 3.38$) at 25°C . (○, $0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4$; Δ, $0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4 - 0.001 \text{ N KCl}$; ●, $0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4 - 0.1 \text{ N KCl}$)

IV. DISCUSSION

None of the work to date has given a clear picture of the mechanism of the anodic dissolution of molybdenum. Information that has been reported is that of Besson and Drautzburg (3) who proposed an initial mean valence of approximately +6 for molybdenum dissolving anodically in 1.0 N H_2SO_4 ; that of Pozdeeva (5) who found a multi-layered film (containing β , β' , and γ phase oxides) formed on the electrode surface during polarization in 1.0 N H_2SO_4 ; and that of Lavrenko and Pen'kov (4) who reported the formation of a thick many-layered oxide film containing MoO_2 and MoO_3 during the anodic oxidation in saturated boric acid solutions.

This work was undertaken to obtain further information pertaining to the anodic dissolution of molybdenum in sulfuric acid solutions ($\text{pH} = 0.38 - 3.38$) which could lead to a better understanding of the dissolution phenomena and check some of the existing theories on the dissolution.

The dissolution in all solutions yielded valences that were independent of pH in the range studied and which did not depart significantly from the valence +6. This is somewhat surprising as Mo^{+3} is the thermodynamically stable species over a large part of the potential region covered and has been predicted to be the product at low current densities. (8) Gas evolution at the molybdenum anode was not observed, even at high current densities. This observation and the +6 valences have been reported by other investigators. (3, 5) The various chloride ion additions (0.001 to 0.1 N) had no effect on the apparent valence.

During the anodic dissolution in all solutions, a dark blue molybdenum oxide film was formed on the electrode. The thickness of the film appeared to increase with increasing current density. At high current densities, the film spalled off the electrode surface, and the electrolyte became dark blue in color. The metal surface beneath the film was smooth and unpitted at all current densities. Several pictures of the film-free metal surface are shown in Figures 10 to 12.

X-ray diffraction analyses of the oxide films were also attempted. The diffraction patterns showed them to be very amorphous. The pattern of the film formed in 1.0 N H_2SO_4 at $0.001 \text{ ma}\cdot\text{cm}^{-2}$ is shown in Figure 13. Due to the diffuseness and low intensity of the lines, only a limited number of d-spacings of an approximate nature could be determined. These could be attributed to either the γ -phase ($\text{MoO}_{2.65}$ - $\text{MoO}_{2.75}$) or the β -phase ($\text{MoO}_{2.87}$) (5) which are similar.* Therefore, the x-ray analyses allow no choice to be made as to the exact nature of phase present which could possibly be a mixture of both γ and β -phases. The amorphous nature could result from the film containing relatively large amounts of H_2MoO_4 or other hydrated oxides whose compositions fall within the limits $\text{MoO}_{2.5}$ to MoO_3 .

Polarization measurements on the molybdenum anode were made in various electrolytes. From the potential-current density plots, linear (Tafel) relationships were found in the potential region up to approximately 150 mv above

*The molybdenum compounds usually associated with these phases are Mo_2O_5 and Mo_4O_{11} whose structures are well known.

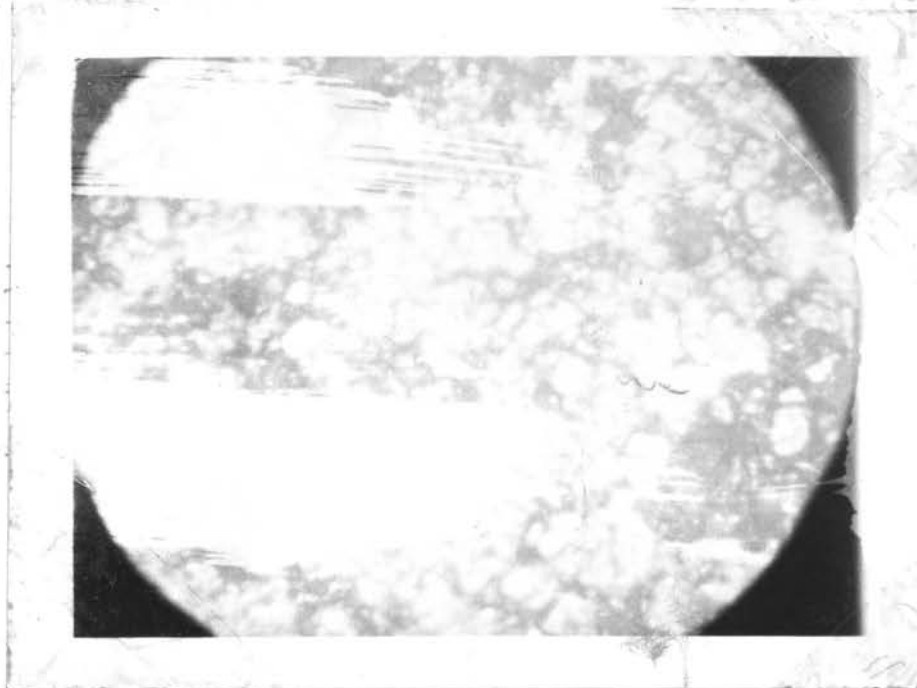


Figure 10. The film-free molybdenum surface after anodic dissolution in 1.0 N H_2SO_4 (no Cl^- present).



Figure 11. The film-free molybdenum surface after anodic dissolution in 1.0 N H_2SO_4 -0.001 N KCl (pH = 0.38) solution.

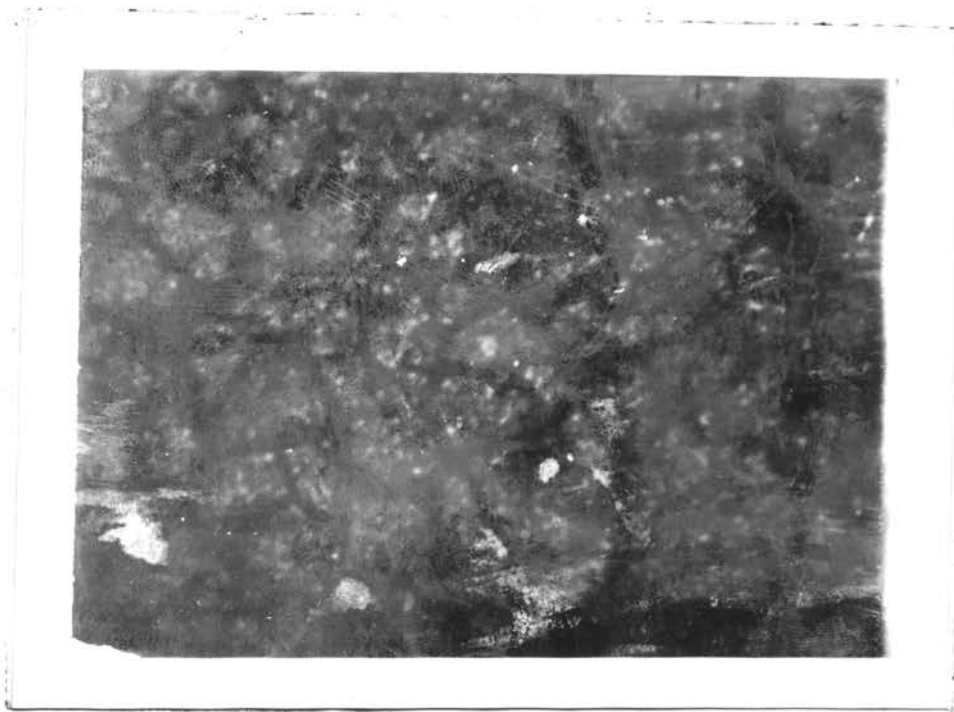


Figure 12. The film-free molybdenum surface after anodic dissolution in 1.0 N H_2SO_4 -0.1 N KCl (pH = 0.38) solution.

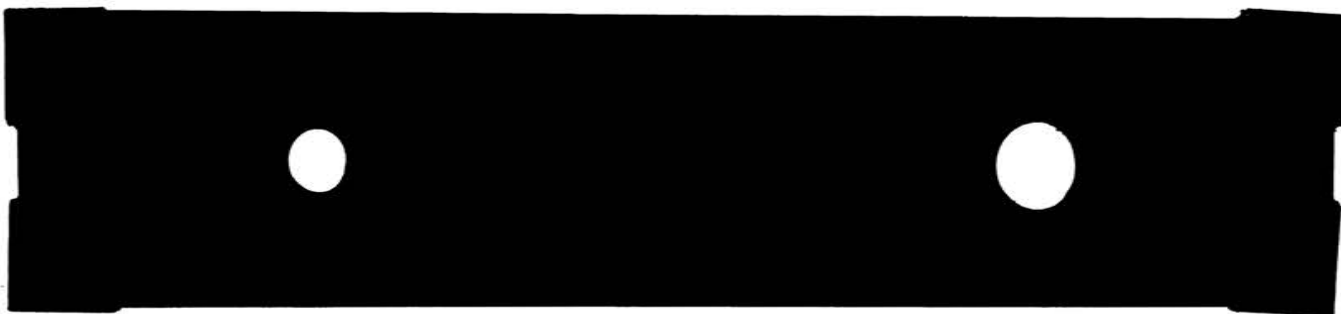


Figure 13. X-ray diffraction patterns of the film formed on the molybdenum anode in 1.0 N H_2SO_4 at $0.001 \text{ ma} \cdot \text{cm}^{-2}$.

the rest potential. The Tafel slopes were relatively independent of the pH as was also the dissolution rate. The Cl^- ion concentration had no noticeable effect on the polarization curves. A summary of the Tafel slopes and rest potentials is given in Table II.

Slightly above the Tafel region, the current density was constant or decreased somewhat with increasing potential. At potentials over 0.70 v, the current continued to increase with increasing potential, although in an erratic manner.

Two polarization techniques were used in 1.0 N H_2SO_4 solution. For the first, each data point was taken after a 15 minute period of approximate steady state current. In the second, at least 30 minutes of steady state operation was allowed before changing the potential. Using this method, a passivation region in 1.0 N H_2SO_4 was observed from 0.47 to 0.55 volts. This could be due to a time-dependent thickening of a protective film or slow formation of a passivating film on the surface (5). The polarization curves and the data for these two runs are shown in Figures 6 and 14 and Tables XIV and XXVI, Appendix D.

The Tafel slopes in H_2SO_4 solutions (pH = 0.38 and 1.38) and H_2SO_4 - K_2SO_4 (pH = 1.50) solutions were approximately 0.060 volts. These are associated with an electrochemical mechanism in which a charge transfer step is followed by a rate-determining chemical reaction step.

According to the experimental data and the x-ray diffraction patterns of the oxide film, the rapid formation of a Mo_2O_5 film is proposed when the electrode is first immersed in the electrolyte. This reaction is shown by the

TABLE II

TAFEL SLOPES AND REST POTENTIALS FOR THE ANODIC DISSOLUTION OF MOLYBDENUM

IN H_2SO_4 - K_2SO_4 SOLUTIONS AT 25°C

Electrolyte	pH	Tafel Slope	Rest Potential
		Volts	Volts (SHE)
1.0 N H_2SO_4	0.38	0.060	0.344
1.0 N H_2SO_4 -0.001 N KCl	0.38	0.054	0.342
1.0 N H_2SO_4 -0.1 N KCl	0.38	0.058	0.351
0.1 N H_2SO_4 -0.001 N KCl	1.38	0.055	0.344
0.1 N H_2SO_4 -0.1 N KCl	1.38	0.061	0.349
0.240 N H_2SO_4 -0.760 N K_2SO_4	1.50	0.065	0.323
0.240 N H_2SO_4 -0.760 N K_2SO_4 - 10^{-3} N KCl	1.50	0.065	0.327
0.240 N H_2SO_4 -0.760 N K_2SO_4 -0.1 N CKl	1.50	0.070	0.327
0.005 N H_2SO_4 -0.995 N K_2SO_4	3.38	0.075	0.298

TABLE II (continued)

Electrolyte	pH	Tafel Slope	Rest Potential
		Volts	Volts (SHE)
0.005 N H ₂ SO ₄ -0.995 N K ₂ SO ₄ -10 ⁻³ N KCl	3.38	0.078	0.282
0.005 N H ₂ SO ₄ -0.995 N K ₂ SO ₄ -0.1 N KCl	3.38	0.077	0.300

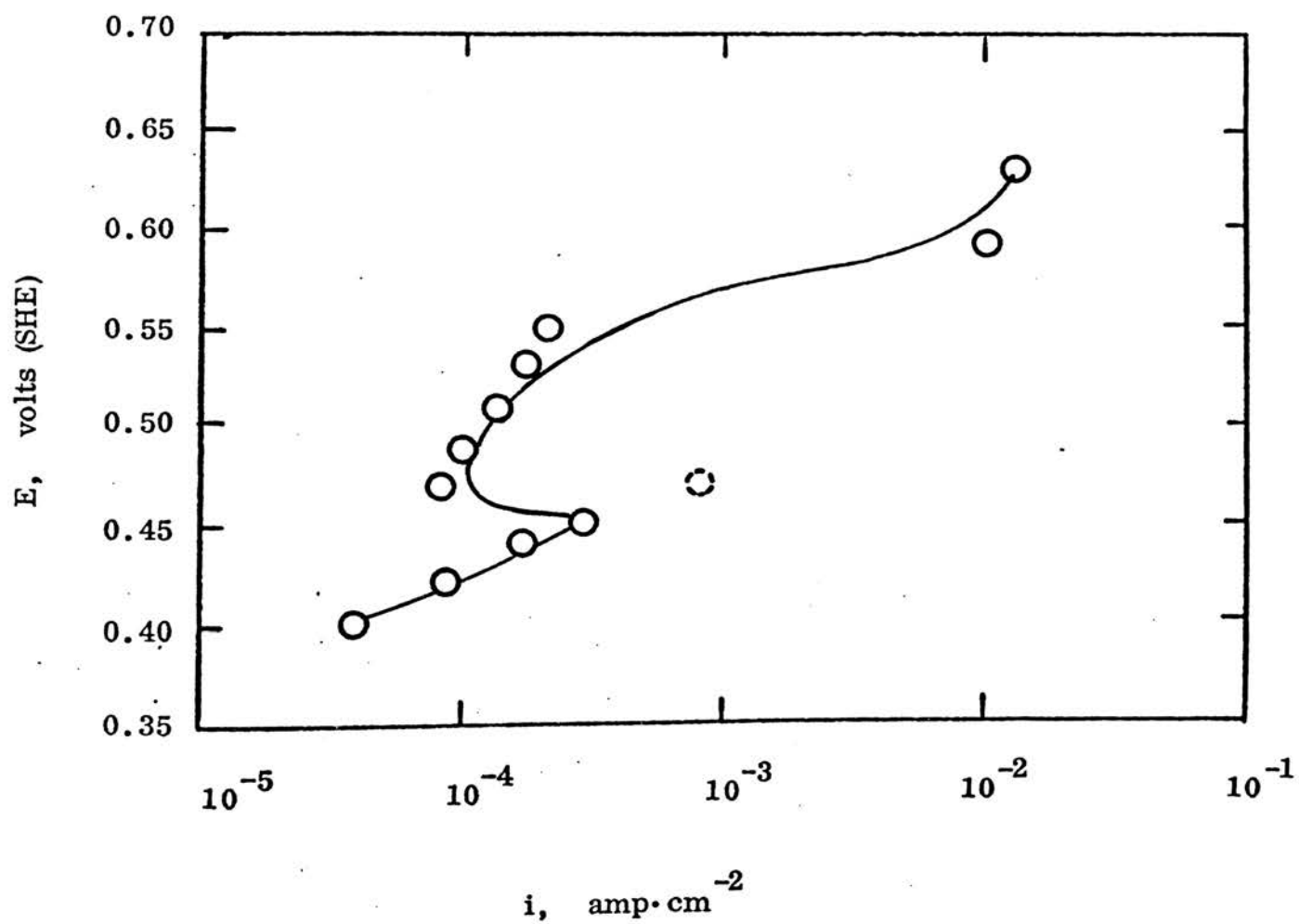
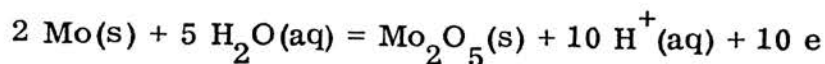
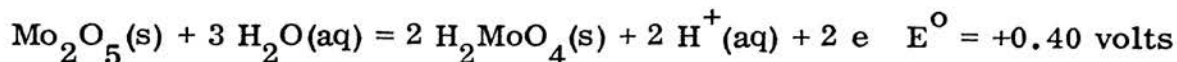


Figure 14. Tafel curve for the anodic dissolution of molybdenum in 1.0 N H₂SO₄ (pH = 0.38) at 25°C.

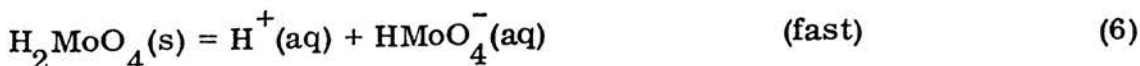
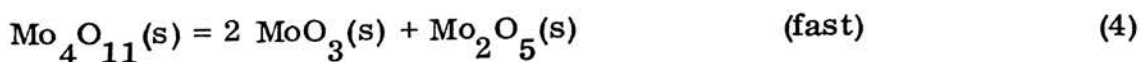
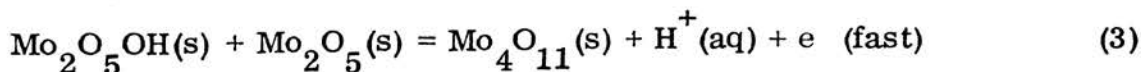
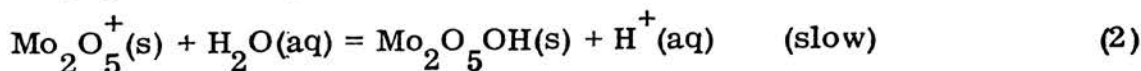
equation



This reaction is substantiated by the rest potential -pH relationship as shown in Figure 15.* It further shows that the most probable overall electrochemical reaction is:



These indicate that the observed kinetic parameters begin with steps associated with the dissolution of Mo_2O_5 and end with the formation of H_2MoO_4 . The species in solution result from the solubility of this final compound. The mechanism can thus be postulated to be



The rate equations for steps 1 and 2 can be formulated as shown in

equations 7 and 8.

$$i_1 = Fk_1 \theta_{\text{Mo}_2\text{O}_5} \exp[(1-\alpha)FV/RT] - Fk'_1 \theta_{\text{Mo}_2\text{O}_5^+} \exp(-\alpha FV/RT) \quad (7)$$

$$i_2 = Fk_2 \theta_{\text{Mo}_2\text{O}_5^+}^a \text{H}_2\text{O} \quad (8)$$

where,

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

*Data for pH = 9.5 - 13.6 from work of C. H. Chi. (13)

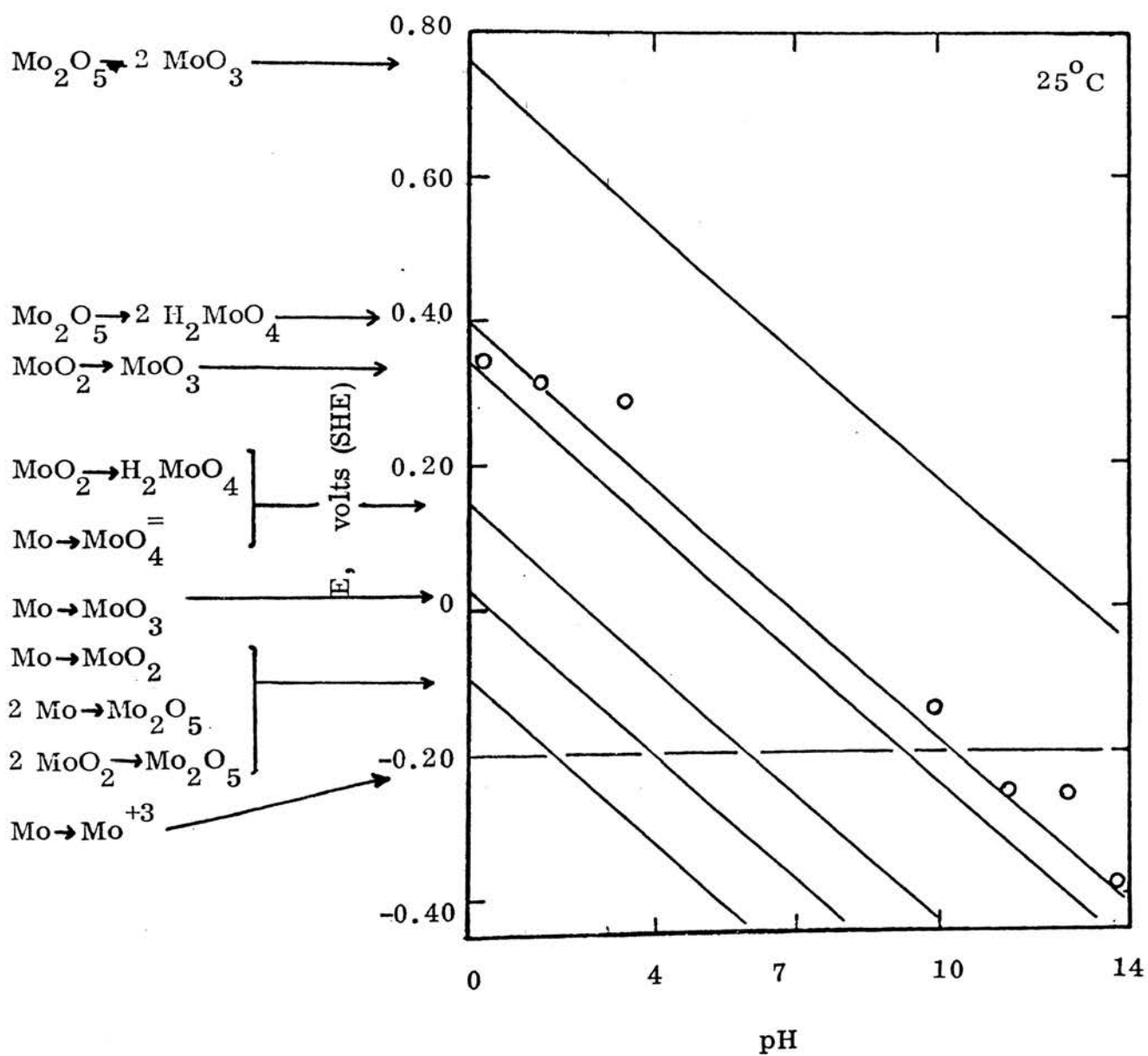


Figure 15. Potential-pH relationship for various electrochemical reactions involving molybdenum and molybdenum oxides at 25°C.

θ = fractional surface coverage of indicated species

α = symmetry factor, assumed to be 0.5

a = activity

k = rate constant

K = equilibrium constant

F = Faraday's constant = 96,486 coulombs/equivalent

V = electrode potential, volts (SHE)

R = gas constant = 8.314 joules/gm-mole^oK

T = temperature, ^oK

Assuming equation (1) to be at equilibrium,

$$\theta_{\text{Mo}_2\text{O}_5^+} = K_1 \theta_{\text{Mo}_2\text{O}_5} \exp(FV/RT) \quad (9)$$

Substituting equation (9) into equation (8),

$$i = i_2 = Fk_2 K_1 \theta_{\text{Mo}_2\text{O}_5} a_{\text{H}_2\text{O}} \exp(FV/RT) \quad (10)$$

This equation shows the correct Tafel slope (0.059 v at 25^oC) and also the pH independence as observed experimentally.

The semi-passivation of molybdenum is proposed as being due to the accumulation of Mo₄O₁₁ on the electrode surface at potentials up to 0.50 v. Above this potential where the current again increases, it appears that the Mo₂O₅ may react directly with H₂O (or OH⁻) to produce MoO₃ that finally leads to the limiting currents.

The layer of trioxide with its high resistivity would preclude reaching potentials necessary for the evolution of oxygen.

V. ACCURACY AND REPRODUCIBILITY

For the valence determinations, the accuracy depended on measurements of the current, time of electrolysis, and the weight-loss of the molybdenum. The time of electrolysis was recorded within ± 1.0 second, giving a maximum error of ± 0.5 percent. The accuracy of the current measured depended on the scale of the milliammeter and could be estimated at ± 2.0 percent. The weight losses were measured with a high sensitivity balance which could introduce a relative error of ± 0.2 percent. The overall reproducibility can therefore, be estimated at approximately ± 3.0 percent.

For the current density-potential measurements, the reproducibility was within ± 15.0 percent.

VI. RECOMMENDATIONS

In this study, experiments indicated that the anodic dissolution rates of molybdenum are relatively independent of pH (from 0.38 to 3.38) and Cl^- in sulfuric acid solutions.

It is recommended that studies at various molybdenum ion concentrations, keeping the other ion concentrations constant, be made to see if there is an influence of the molybdenum ion on the anodic dissolution.

The anodic dissolution of molybdenum in other acids, such as HNO_3 , HCl , HI , etc., and bases, such as NaOH , $\text{Ca}(\text{OH})_2$, would yield valuable data that would be of interest in evaluating its corrosion properties.

VII. APPENDICES

A. Materials.

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

1. Sulfuric Acid. Reagent grade, meets ACS specifications.

Mallinckrodt Co., New York.

2. Potassium Sulfate. Reagent grade, meets ACS specifications.

Fisher Scientific Co., Fairlawn, New Jersey.

3. Potassium Chloride. Reagent grade, meets ACS specifications.

Mallinckrodt Co., New York.

4. Nitrogen. Prepurified grade, Matheson Co., Joliet, Illinois.

5. Molybdenum. One inch rod, 99.9% purity. Typical impurities (ppm):

C, 150; O, 360; Al, <10; Cu, <10; Co, <10; Cr, <10; Fe, <10;

H, <10; N, <10; Ni, <10. Electronic Space Products Inc.,

Los Angeles, California.

B. Equipment.

The following is a list of the principal equipment components used in this investigation.

1. Surface Preparation of Molybdenum Specimens.

- a. Belt Surfacer. Buehler No. 1250. Buehler Ltd., Evanston, Illinois.
- b. Hand Grinder. Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Evanston, Illinois.

2. Electrolysis Apparatus.

- a. Power Supply. Sorensen, QRB(40 v, 0.75 amp) D.C. power supplies. Raytheon Co., South Norwalk, Connecticut.
- b. Power Supply. PP-351/U, 150 v, 0.1 amp D.C. Foto-Video Electronics Inc., Cedar Grove, New Jersey.
- c. Electrometer. Multi-range type, Model 610 B, Keithley Instruments Inc., Cleveland, Ohio.
- d. Ammeter. Ultra high sensitivity volt-ohm-microammeter, Simpson 269, Simpson Electric Co., Chicago, Illinois.
- e. Potentiostat. Anotrol, Model 4100, Anotrol Division of Continental Oil Co., Ponca City, Oklahoma.
- f. Strip Chart Recorder. Model 7100A. Autograph, F. L. Moseley Co., Pasadena, California.
- g. Temperature Controller. Model 115, Proportional Temperature Control, Fisher Scientific Co., Fairlawn, New Jersey.
- h. Balance. Type 121211, Sartorius-Werke Co., Germany.

C. Tables III to XII, APPARENT VALENCE MEASUREMENTS.

(anodic area = 2.8353 cm^{-2} unless otherwise specified)

TABLE III

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

 $1 \text{ N H}_2\text{SO}_4$ (pH = 0.38) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0338	0.0339	5.98
28,800	0.003	0.0406	0.0410	5.94
9,000	0.010	0.0422	0.0424	5.97
3,600	0.030	0.0507	0.0511	5.95
1,200	0.100	0.0564	0.0569	5.94

TABLE IV

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

1 N H₂SO₄ - 10⁻³ N KCl (pH = 0.38) at 25°C

t	i	W _a	W _e	V _i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0337	0.0339	5.96
28,800	0.003	0.0405	0.0406	6.01
9,000	0.010	0.0422	0.0419	6.04
3,600	0.030	0.0507	0.0507	6.00
*1,200	0.100	0.0156	0.0150	6.00

*area = 0.7584 cm²

TABLE V

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

1 N H₂SO₄-0.1 N KCl (pH = 0.38) at 25^oC

t	i	W _a	W _e	V _i
sec	amp cm ⁻²	gm	gm	
72,208	0.001	0.0339	0.0341	5.96
28,800	0.003	0.0406	0.0403	6.04
9,000	0.010	0.0422	0.0424	5.97
3,600	0.030	0.0507	0.0507	6.00
*1,200	0.100	0.0156	0.0155	6.01

*area = 0.7584 cm²

TABLE VI

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.1 N H_2SO_4 - 10^{-3} N KCl (pH = 1.38) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0338	0.0351	5.77
28,800	0.003	0.0406	0.0420	5.80
9,000	0.010	0.0422	0.0435	5.83
3,600	0.030	0.0507	0.0522	5.83
*1,200	0.100	0.0156	0.0158	5.92

*area = 0.7584 cm²

TABLE VII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.1 N H₂SO₄-0.1 N KCl (pH = 1.38) at 25^oC

t	i	W _a	W _e	V _i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0338	0.0337	6.01
43,200	0.003	0.0609	0.0612	5.97
9,000	0.010	0.0422	0.0424	5.98
3,600	0.030	0.0507	0.0512	5.94
*1,200	0.100	0.0156	0.0155	6.03

*area = 0.7584 cm²

TABLE VIII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.240 N H_2SO_4 -0.760 N K_2SO_4 (pH = 1.50) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0338	0.0341	5.94
28,800	0.003	0.0406	0.0409	5.95
9,000	0.010	0.0422	0.0430	5.90
3,600	0.030	0.0507	0.0513	5.93
*1,200	0.100	0.0156	0.0157	5.96

*area = 0.7584 cm²

TABLE IX

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.005 N H_2SO_4 - 0.995 N K_2SO_4 (pH = 3.38) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
72,000	0.001	0.0338	0.0341	5.95
28,800	0.003	0.0406	0.0410	5.94
9,000	0.010	0.0422	0.0418	6.05
3,600	0.030	0.0507	0.0511	5.95
*1,200	0.100	0.0156	0.0154	6.07

*area = 0.7584 cm²

TABLE X

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

$$0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4 - 10^{-3} \text{ N KCl (pH = 3.38) at } 25^\circ\text{C}$$

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
28,800	0.003	0.0406	0.0417	5.84
3,600	0.030	0.0507	0.0518	5.87

TABLE XI

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

$$0.240 \text{ N H}_2\text{SO}_4 - 0.760 \text{ N K}_2\text{SO}_4 - 10^{-3} \text{ N KCl (pH = 1.50) at } 25^\circ\text{C}$$

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
28,800	0.003	0.0406	0.0409	5.95
3,600	0.030	0.0507	0.0513	5.93

TABLE XII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.240 N H_2SO_4 - 0.760 N K_2SO_4 - 0.1 N KCl (pH = 1.50) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
28,800	0.003	0.0406	0.0411	5.93
3,600	0.030	0.0507	0.0511	5.95

TABLE XIII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN

0.005 N H_2SO_4 - 0.995 N K_2SO_4 - 0.1 N KCl (pH = 3.38) at 25°C

t	i	W_a	W_e	V_i
sec	amp·cm ⁻²	gm	gm	
28,800	0.003	0.0406	0.0414	5.88
3,600	0.030	0.0507	0.0506	6.01

D. TABLES XIV TO XXVI, POLARIZATION MEASUREMENTS.

TABLE XIV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 1 N H_2SO_4 (pH = 0.38) at 25°C

E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp·cm ⁻²
0.344	0.000	0.000
0.382	0.017	0.008
0.422	0.135	0.067
0.442	0.35	0.175
0.462	0.94	0.47
0.482	4.83	2.415
0.502	14	7
0.522	22.2	11.1
0.542	22	11
0.562	36.7	18.35
0.582	67.2	33.6
0.602	107	53.5
0.622	128	64.

Area = 2 cm²

TABLE XV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 1 N H₂SO₄-10⁻³N KCl (pH = 0.38) at 25^oC

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp·cm ⁻²
0.342	0.000	0.000
0.402	0.051	0.025
0.422	0.13	0.065
0.432	0.222	0.111
0.442	0.353	0.176
0.452	0.575	0.287
0.462	0.92	0.46
0.482	5.5	2.75
0.502	13.2	6.6
0.522	26	13
0.542	26*	13*
0.562	30	15
0.582	54	27
0.602	73	36.5
0.622	101	50.5
0.642	104	52

Area = 2 cm²

* = Current kept increasing

TABLE XVI

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 1 N H₂SO₄-0.1 N KCl (pH = 0.38) at 25^o C

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp·cm ⁻²
0.351	0.000	0.000
0.401	0.037	0.075
0.421	0.12	0.24
0.441	0.2	0.4
0.461	0.395	0.79
0.481	0.9	1.8
0.501	1.55	3.1
0.531	5.3	10.6
0.551	12	24
0.571	16.7	33.4
0.591	20	40
0.611	14.5	29
0.631	23	46

Area = 0.5 cm²

TABLE XVII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 0.1 N H₂SO₄-10⁻³ N KCl (pH = 1.38) at 25^oC

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp·cm ⁻²
0.344	0.000	0.000
0.402	0.032	0.032
0.422	0.064	0.064
0.442	0.184	0.184
0.462	0.502	0.402
0.482	0.99	0.99
0.502	2.1	2.1
0.522	4.6	4.6
0.542	5.65 **	0.65 **
0.562	7.35	7.35
0.582	13.1	13.1
0.602	20.2	20.2

Area = 1 cm²

** = Current kept decreasing

TABLE XVIII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN 0.1 N H₂SO₄-0.1 N KCl (pH = 1.38) at 25° C

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp·cm ⁻²
0.349	0.000	0.000
0.402	0.056	0.028
0.422	0.107	0.053
0.442	0.245	0.122
0.462	0.55	0.275
0.482	1.02	0.51
0.502	2.45	1.225
0.522	3	1.5
0.542	3	1.5
0.562	3.25	1.625
0.582	3.41	1.705
0.602	3.67	1.835
0.622	3.55	1.775
0.650	8	4
0.672	21	10.5
0.692	17.2	8.6
0.712	13.8	6.9
0.732	17	8.5
0.752	20	10

Area = 1 cm²

TABLE XIX

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 0.240 N H₂SO₄-0.760 N K₂SO₄ (pH = 1.50) at 25^oC

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp · cm ⁻²
0.323	0.000	0.000
0.373	0.015	0.015
0.402	0.04 **	0.04 **
0.422	0.091	0.091
0.442	0.222	0.222
0.462	0.42	0.42
0.482	0.835	0.835
0.502	1.63	1.63
0.522	2.8	2.8
0.542	2.2	2.2
0.562	2.2	2.2
0.582	2.4	2.4
0.602	2.53	2.53
0.622	2.6	2.6
0.642	2.6	2.6
0.662	2.6	2.6
0.682	7.4	7.4
0.702	7.2	7.2
0.722	15.2	15.2

Area = 1 cm²

** = Current kept decreasing

TABLE XX

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN 0.240 N H_2SO_4 -0.760 N K_2SO_4 - 10^{-3} N KCl at 25°C
 (pH = 1.50)

E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp · cm ⁻²
0.327	0.000	0.000
0.452	0.25	0.25
0.472	0.52	0.52
0.492	0.95	0.95
0.512	1.72	1.72
0.542	2.1	2.1
0.562	2	2
0.592	2.1	2.1
0.612	2.2	2.2
0.632	2.2	2.2
0.652	2.2	2.2
0.682	2.2	2.2
0.712	7.3	7.3
0.742	8.5	8.5
0.772	14.8	14.8
0.802	22.8	22.8
0.832	40.8	40.8
0.862	51	51

Area = 1 cm²

TABLE XXI

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN 0.240 N H_2SO_4 -0.760 N K_2SO_4 -0.1 N KCl at 25^o C
 (pH = 1.50)

E volts (SHE)	$I \times 10^3$ amps	$i \times 10^3$ amp cm^{-2}
0.327	0.000	0.000
0.432	0.14	0.14
0.452	0.36	0.36
0.472	0.675	0.675
0.492	1.24	1.24
0.512	2.23	2.23
0.532	3.75	3.75
0.552	3.45 **	3.45 **
0.572	2.7 **	2.7 **
0.592	2.75	2.75
0.612	2.8	2.8
0.632	2.8	2.8
0.652	2.8	2.8
0.672	3.65	3.65
0.692	9.4	9.4
0.712	7	7
0.732	12.4	12.4
0.752	30*	30*
0.772	40.5	40.5
0.792	47.5	47.5

Area = 1 cm^2

* = Current kept increasing

** = Current kept decreasing

TABLE XXII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF

MOLYBDENUM IN 0.005 N H_2SO_4 -0.995 N K_2SO_4 (pH = 3.38) at 25^oC

E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp·cm ⁻²
0.298	0.000	0.000
0.352	0.072	0.072
0.382	0.203	0.203
0.402	0.342	0.342
0.422	0.5	0.5
0.442	0.7	0.7
0.472	0.97	0.97
0.492	1.09	1.09
0.522	1.38	1.38
0.552	0.75 **	0.75 **
0.572	0.65	0.65
0.602	1	1
0.622	1.36	1.36
0.652	2.3	2.3
0.682	4	4
0.702	6.4	6.4
0.732	5.18	5.18
0.762	10.05 *	10.05 *
0.802	25	25
0.852	32	32
0.902	38	38

TABLE XXII continued

E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp·cm ⁻²
0.922	39	39
0.952	42	42
0.982	44	44
1.002	45.9	45.9

Area = 1 cm²

* = Current kept increasing

** = Current kept decreasing

TABLE XXIII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN $0.005 \text{ N H}_2\text{SO}_4 - 0.995 \text{ N K}_2\text{SO}_4 - 10^{-3} \text{ N KCl}$ at 25°C
 (pH = 3.38)

E	$I \times 10^3$	$i \times 10^3$	E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp · cm ⁻²	volts (SHE)	amps	amp · cm ⁻²
0.282	0.000	0.000	0.6	0.632	1.55
0.302	0.016	0.016	0.662	2.14	2.14
0.332	0.045	0.045	0.702	2.93	2.93
0.352	0.085	0.085	0.732	4.52	4.52
0.382	0.18	0.18	0.752	4.88	4.88
0.402	0.28	0.28	0.782	8.2	8.2
0.432	0.53	0.53	0.812	20.2	20.2
0.452	0.9	0.9	0.852	31	31
0.482	1.32	1.32	0.892	33	33
0.512	1.55	1.55	0.932	31	31
0.532	1.7	1.7	1.002	28	28
0.562	1.92	1.92	1.052	28	28
0.582	1.2 **	1.2 **	1.102	29	29
0.602	1.1 **	1.1 **	1.152	30	30

Area = 1 cm²

** = Current kept decreasing

TABLE XXIV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN 0.005 N H₂SO₄-0.995 N K₂SO₄-0.1 N KCl at 25°C
 (pH = 3.38)

E volts (SHE)	I x 10 ³ amps	i x 10 ³ amp. cm ⁻²
0.300	0.000	0.000
0.352	0.041	0.041
0.372	0.059	0.059
0.402	0.17	0.17
0.422	0.258	0.258
0.442	0.5	0.5
0.462	0.602	0.602
0.482	0.755	0.755
0.512	1.02	1.02
0.532	1.12	1.12
0.552	1.25	1.25
0.582	1.58	1.58
0.612	1.62	1.62
0.632	1.4	1.4
0.652	1.55	1.55
0.672	1.98	1.98
0.702	4.12	4.12
0.732	5.75 **	5.75 **
0.762	8.5	8.5

Area = 1 cm²

** = Current kept decreasing

TABLE XXV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
 MOLYBDENUM IN 1 N H₂SO₄ (pH = 0.38) at 25^oC
 BY THE GALVANSTATIC TECHNIQUE

E	$I \times 10^3$	$i \times 10^3$
volts (SHE)	amps	amp·cm ⁻²
0.344	0.000	0.000
0.452	0.3	0.3
0.464	0.6	0.6
0.469	0.8	0.8
0.474	1	1
0.517	3	3
0.535	6	6
0.559	10	10
0.597	20	20
0.652	40	40
0.712	80	80
0.767	140	140
0.788	200	200

Area = 1 cm²

TABLE XXVI

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF
MOLYBDENUM IN 1 N H₂SO₄ (pH = 0.38) at 25^oC

E	I x 10 ³	i x 10 ³
volts (SHE)	amps	amp·cm ⁻²
0.348	0.000	0.000
0.402	0.042	0.042
0.422	0.084	0.084
0.442	0.189	0.189
0.452	0.31	0.31
0.472	0.085	0.085
0.492	0.1	0.1
0.512	0.14	0.14
0.532	0.18	0.18
0.552	2.25	2.25
0.592	10.5	10.5
0.632	13.5	13.5

Area = 1 cm²

BIBLIOGRAPHY

1. Cotton, F. Albert, and G. Wilkison, "Advanced Inorganic Chemistry". Interscience Publisher, New York, 776 (1962).
2. Jones, E. S., J. F. Mosher, Rudolph Speiser, and J. W. Spretnak, Corrosion, 14, 20 (1958).
3. Besson, J., and G. Drautzburg, Electrochim Acta, 3, 158 (1960).
4. Lavenko, V. A., and A. A. Penkov, Zh, fiz. Khim. 37, 1049 (1963).
5. Pozdeeva, A. A., E. I. Antenevskya, and A. M. Sukhotia, Corrosion Science, 6, 149 (1966).
6. Mashing, G., and G. Roth: Werkstoffe Korros. Mannheim. H5-6, 176 (1952).
7. Shatalov, A. Ya., and I. A. Marshakov, Zh, fiz. Khim. 28, 42 (1954).
8. Boss, H. J. Werkstoffe Korros. H9, 538 (1962).
9. Bardin, V. V., "The Investigation of Molybdenum and Molybdenum Oxide Electrodes and Their Use in Potentiometric Analyses", Dissertation. L.T.I., Leningrad. (1958).
10. Rudiger, O., and R. Fischer, Electrochem. 62, 805 (1958).
11. Heuman, Voh Th., and G. Hauck: Eingegangen am 19, Januar, (1967).
12. Chi, C. H., "Anodic Dissolution of Molybdenum in Alkali Solutions." Unpublished thesis, University of Missouri - Rolla.
13. Johnson, J. W., J. L. Reed, and W. J. James, J. Electrochem. Soc., 114, 572 (1967).

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