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THE ANODIC DISSOLUTION OF MOLYBDENUM IN ALKALINE SOLUTIONS

BY

CHEN-HWEI CHI, 1941

440

A

THESIS

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Approved by

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ABSTRACT

The purpose of this investigation was to study the anodic behavior of molybdenum in alkaline solutions, pH 9.5 - 13.6.

The investigation led to the following conclusions:

(1) Molybdenum is oxidized to the +6 state, relatively independent of current density from $10^{-3}<i<10^{-1}$ amp$\cdot$cm^{-2}.

(2) The resultant ions in solution are $MoO_4^=$.

(3) There is no significant Cl^- effect $(10^{-5}<c_{Cl^-}<10^{-1})$ on the dissolution.

The proposed dissolution mechanism is:

$2\ Mo(s) + 5\ OH^-(aq) = Mo_2O_5(s) + 5\ H^+(aq) + 10\ e$ (1)

$Mo_2O_5(s) + OH^-(aq) = Mo_2O_5OH(s) + e$ (2)

$Mo_2O_5OH(s) + Mo_2O_5(s) = Mo_4O_{10}OH(s)$ (3)

$Mo_4O_{10}OH(s) = Mo_4O_{11}(s) + H^+(aq) + e$ (4)

$Mo_4O_{11}(s) = 2\ MoO_3(s) + Mo_2O_5(s)$ (5)

$MoO_3(s) + H_2O(aq) = H_2MoO_4(s)$ (6)

$H_2MoO_4(s) + 2\ OH^-(aq) = MoO_4^=(aq) + 2\ H_2O(aq)$ (7)

In KOH solution, equation (3) appears to be the slow step. As the pH is lowered (K_2CO_3 solution), equation (2) becomes rate determining. Limiting currents in KOH solution appear to result from the dissolution of MoO_3 which is formed on the surface at high potentials and which is unstable in alkaline media.

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NOTATION

A = Atomic weight of molybdenum = 95.95 gm

a = Activity

E_o = Standard potential, volts (SHE)

F = Faraday constant = 96,486 coulombs/gm·equiv.

I = Current, amps

i = Current Density, amp·cm^{-2}

k = Constant

n = Normal cationic charge of molybdenum = +6

R = Gas constant = 8.314 joules/gmole K°

T = Temperature, °K

t = Time, sec

V = Potential, volts (SHE)

Z_i = Apparent valence

W_a = Theoretical weight-loss of molybdenum, gm

W_e = Experimental weight loss , gm

Θ = Fractional surface coverage

I. INTRODUCTION

Details concerning the anodic dissolution of many metals in various solutions are still unknown. Discrepancies are found between the actual weight-loss of an electrode and that calculated from coulometric data. The purpose of this investigation was to study the anodic dissolution of molybdenum (Mo) in basic solutions to determine the apparent valence of Mo ions going into solution, the nature of any surface films formed during dissolution, and the polarization behavior.

Three electrolytes were used: 1 N potassium hydroxide (pH = 13.6), 0.667 N potassium carbonate (pH = 11.5), and potassium carbonate-potassium sulfate mixture (pH = 9.5). Chloride ion additions were also made to determine their effect on both the current efficiency and the polarization behavior.

II. LITERATURE REVIEW

The literature review for this investigation is divided into two parts (a) current efficiencies and (b) polarization of molybdenum during anodic dissolution in aqueous solutions.

A. Current Efficiency of the Anodic Dissolution of Molybdenum in Aqueous Solutions.

In 1905, Marino(1) reported that molybdenum dissolves anodically in the hexavalence state at current densities between 0.005 to 0.050 amp·cm^{-2} in solutions of potassium hydroxide, sodium sulfate and potassium chloride. In 1910, Kuessner(2) found that the anodic current efficiency for the dissolution of molybdenum to molybdate decreased with increasing current density and decreasing temperature in 1 N KOH solution. Both Marino and Kuessner determined current efficiencies by measuring the weight loss of the anode corresponding to the passage of a given quantity of electricity and assuming that the metal was dissolved as molybdate ions ($MoO_4^=$).

In 1939, Thompson and Kaye(3) reported a simultaneous electrolytic oxidation of molybdenum to soluble molybdate and insoluble oxide in potassium hydroxide solutions at 25°C. At high current densities (>0.3 amp·cm^{-2}) and low KOH concentrations (<0.5 N), the oxide product consisted of a mixture of greenish $Mo(OH)_4$ and the colloidal blue Mo_3O_8. They suggested an increased current efficiency with increasing KOH concentration and decreasing current density for molybdate formation according to the reaction

$$Mo + 8\ OH^- = MoO_4^= + 4\ H_2O + 6\ e \quad (8)$$

No oxygen evolution was observed up to current densities of 0.4 $amp \cdot cm^{-2}$. They also suggested that oxygen would be evolved at potentials of 1.6 volts, but this value was never approached in their investigation. In the same year, Morral and Bray(4) reported an apparent valence of 5.85 for molybdenum dissolving anodically at a current density of 0.4 $amp \cdot cm^{-2}$.

Blavatnik, et. al., (5) studied the anodic dissolution of molybdenum in nitric acid at current densities of 1.0 $amp \cdot cm^{-2}$ using compacted plates prepared from powders. They found efficiencies of 115 to 130 percent assuming molybdenum went into solution as Mo^{+6}.

In 1966, Gladysheva and Shatalov(6) studied the effect of pH on the current and weight-loss of Mo anodes in buffer solutions with 0.5 N Cl^-. Mo couples were used in which the catholyte was saturated with oxygen and the anolyte with nitrogen. High current densities corresponding to the dissolution rates were observed only in alkaline solutions. The localization of weight-loss on the anode tended to rise in the pH region in which the current decreased due to passivation.

B. Polarization of Molybdenum During Anodic Dissolution in Aqueous Solutions.

Thompson and Kaye(3) found that the fractional change in the current density for the formation of molybdate corresponding to a given change in electrode potential was less than the fractional change in the current density for the formation of oxide for the same difference in electrode potential. The reason given was that the polarization for the anodic oxidation to molybdate was greater than the polarization for the oxidation to oxide.

Besson and Drautzburg(7) studied the anodic behavior of molybdenum and found the polarization curves to be continuous up to about 0.1 amp$\cdot$cm^{-2}. The shape of the curves was independent of electrolyte pH, but were shifted along the potential axis. They reported abnormally small values of the transfer coefficient (0.1 - 0.2) which was said to depend on the medium, in particular its pH, and was explained by adsorption of anions on the metal surface. They described the metal as being covered with colored films of unknown nature.

Several investigations have been made concerning the electrode potential of molybdenum. Masing and Röth(8) reported that the steady potential depends on the pH of the electrolyte in a manner somewhat analogous to Sb. They calculated the normal potential (E^o) of $Mo/MoO_4^=$ to be 0.17 volts. The anodic dissolution was found to follow the Tafel relation (E = a + b log i) over an appreciable current density range.

Shatalov(9) measured the electrode potentials and corrosion rates of molybdenum in buffered and non-buffered solutions of various pH and Cl^- concentrations. He found a narrow range of irreversible potentials which varied by 0.035 - 0.045 volts/pH unit. Significant corrosion was noted only in alkaline solutions. The presence of Cl^- had only a slight and irregular effect on both the electrode potential and corrosion rate. Later, Shatalov and Marshakov(10) presented a relationship for the steady potential of molybdenum as E = 0.375 - 0.045 pH. For some unbuffered solutions, the potential was almost constant between pH's of 6 to 9. This region was thought to be caused by a saturation of the solution near the electrode with the metal hydroxide.

Recently Pozdeeva, Antonovskaya and Sukhotin(11) studied the passivity of molybdenum in both acid and basic solutions. They found the passivity region in 1 N H_2SO_4 to extend from -0.15 to 0.4 volts where it adjoins the immunity region. There was no passive region in alkaline solutions. No oxygen evolution was observed for over-potentials up to 2.5 volts. In all the potential regions studied, molybdenum entered into solution as $MoO_4^=$ ions. Films were observed on the electrode in both acid and alkaline electrolytes. The lower oxides such as MoO_2 and

Mo_2O_5 were found at $E_o = -0.9$ volts. The formation of the oxides can be represented by the equations:

$$Mo + 4\ OH^- = MoO_2 + 2\ H_2O + 4\ e \qquad E_o = -0.91 \text{ volts} \qquad (9)$$

$$2\ Mo + 10\ OH^- = Mo_2O_5 + 5\ H_2O + 10\ e \quad E_o = -0.90 \text{ volts} \qquad (10)$$

In alkaline solutions, the oxides are unstable and are oxidized to $MoO_4^{=}$ at -0.96 to -1.0 volts as shown by the following equations:

$$MoO_2 + 4\ OH^- = MoO_4^{=} + 2\ H_2O + 2\ e \qquad E_o = -0.96 \text{ volts} \qquad (11)$$

$$Mo_2O_5 + 6\ OH^- = 2\ MoO_4^{=} + 3\ H_2O + 2\ e \quad E_o = -1.01 \text{ volts} \qquad (12)$$

Thus, the inability of molybdenum to passivate in 1 N KOH was attributed to the dissolution of the surface films throughout the potential range in which molybdenum dissolves. The higher oxide MoO_3 is stable in the range between -0.2 to 1.5 volts.

$$Mo + 6\ OH^- = MoO_3 + 3\ H_2O + 6\ e \qquad E_o = -0.77 \text{ volts} \qquad (13)$$

It was concluded that the near constant rate of dissolution of molybdenum at high potentials was due to an outer layer of this oxide.

In 1967, Eidman(12) studied the anodic behavior of molybdenum in sodium hydroxide solutions. He obtained anodic polarization curves as a function of NaOH concentration (0.01 to 1.0 N) and temperature (20 to 80°C). He found the polarization curves to be described by the Tafel equation at low current densities. However, after reaching a certain potential, a limiting current was obtained. The region where current density was independent of potential was described as being limited by the transport of OH^- ions to the electrode.

III. EXPERIMENTAL

The plan of investigation consisted of the following major phases: (1) the effect of current density, pH, and chloride ion on the apparent valence of molybdenum undergoing anodic dissolution in alkaline solutions, and (2) the relationship between current density and potential for the dissolution of molybdenum under the same conditions as phase (1). Films formed during the dissolution processes were studied by microscopic and x-ray diffraction techniques.

A description of the apparatus, the method of procedure, data, results, and sample calculations are included for each phase of the experimentation. Lists of the materials and equipment are given in Appendices A and B.

A. Apparent Valence of Molybdenum Undergoing Anodic Dissolution in Alkaline Solutions.

1. Apparatus. The apparatus consisted of an electrolytic cell with separated compartments of 300 milliliter capacity, a molybdenum anode, a platinized-platinum cathode, a decade power resistor, and a knife-blade switch, all connected in series with a 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 immersed in a water-bath controlled at 25 ± 0.1°C.

2. Procedure. A specimen of known cross-sectional area was cut from a bar of molybdenum metal of 99.9 percent purity. The specimen was polished immediately before each run according to the procedure listed in Appendix C, then dried and weighed as described in the following paragraph. The weighed specimen was mounted in a teflon holder as shown in Figure 2. Approximately 200 milliliters of electrolyte were transferred into the electrolysis cell and the molybdenum anode and the platinized-platinum cathode positioned as shown in Figure 1. The cell was placed into the constant temperature water-bath in such a position as to insure complete submergence of the electrolyte and allowed to come to constant temperature before starting a run. Nitrogen was continuously bubbled through both the anodic and cathodic compartments to remove air and stir the electrolyte.

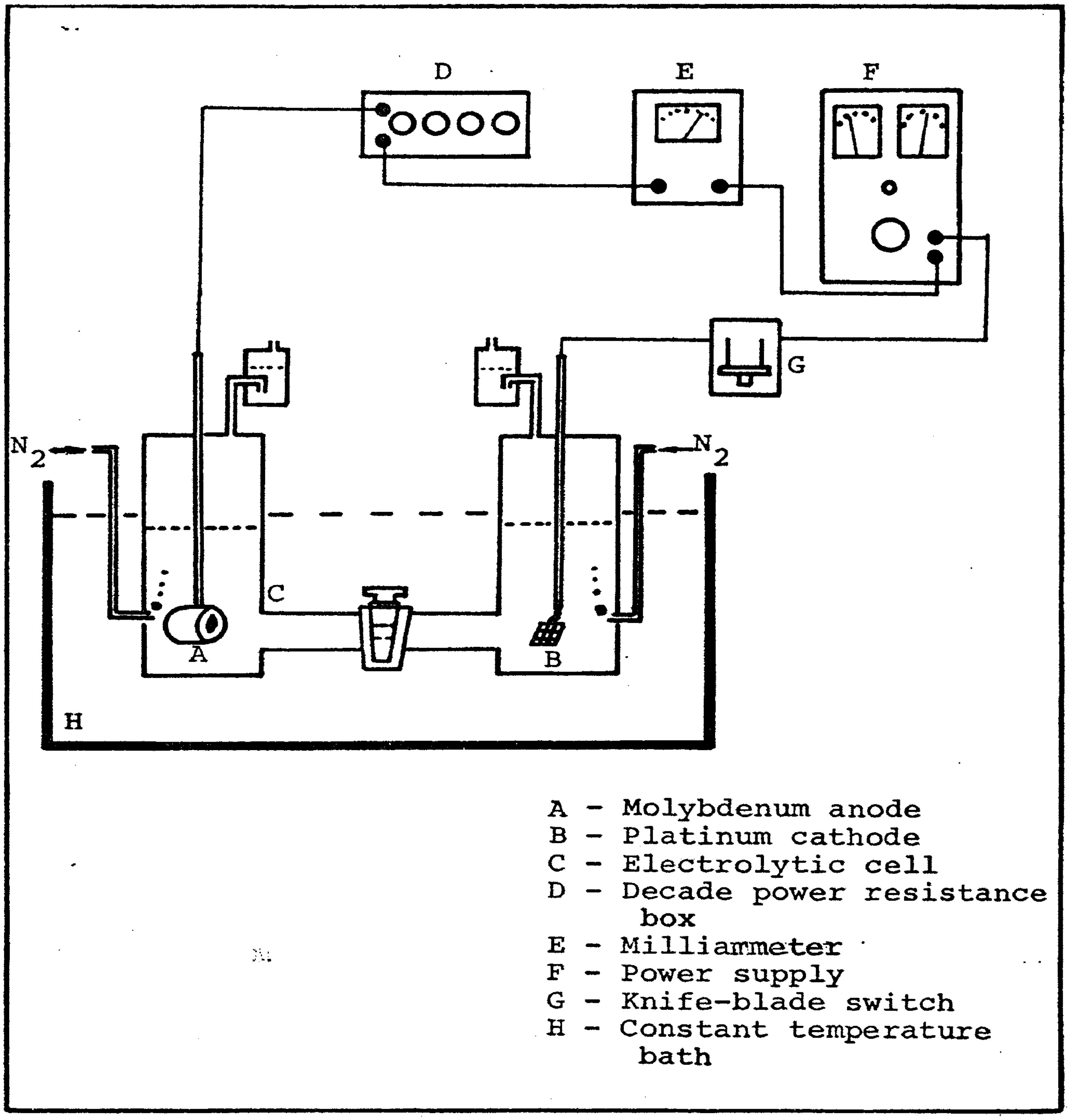

Figure 1. Schematic diagram of the apparatus for the measurement of the apparent valence of molybdenum undergoing anodic dissolution.

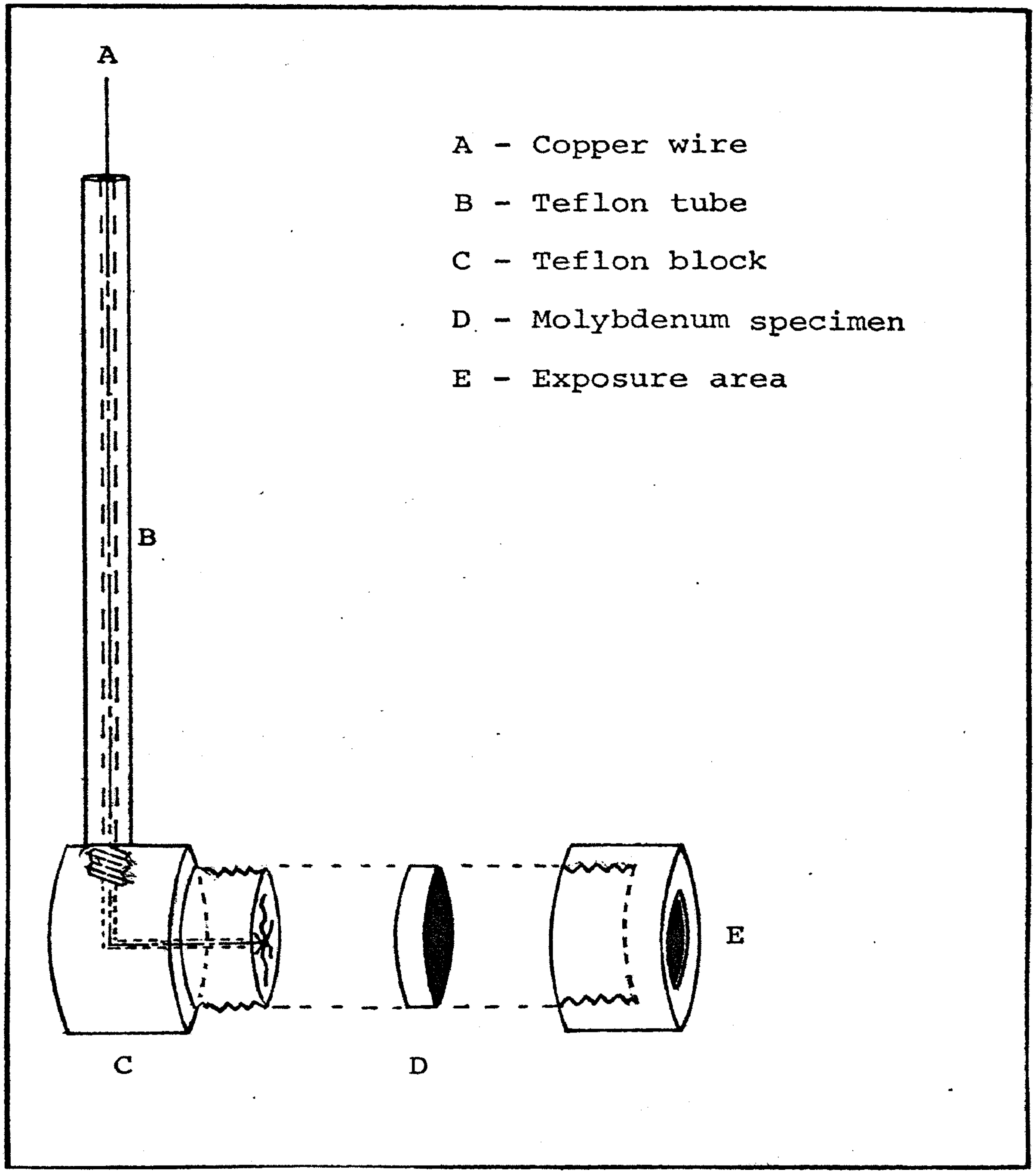

Figure 2. Diagram of the teflon holder of the molybdenum anode for apparent valence measurement.

To begin a run, the power supply was turned on, the output voltage adjusted to a value between 200 and 500 volts, the knife-blade switch closed, and the current adjusted to a desired value by varying the setting of the power resistance. A timer and milliammeter were used to determine the number of coulombs (amps-seconds) passed. After a predetermined time interval had elapsed, the knife-blade switch was opened and the electrodes removed from the cell. The molybdenum surface was scrubbed off with a rubber policeman and saved as described in Appendix C. After removal of the film, the anode was cleaned, dried, put into a dessicator for 8 hours, and reweighed on a balance with a sensitivity of 0.00001 gram to determine the weight loss.

3. Data and Results. The data obtained for the anodic dissolution in the different electrolytes are shown in Tables V to X, Appendix D. . The electrolytes were KOH, K_2CO_3, and $K_2CO_3 + K_2SO_4$ mixtures with and without Cl^- additions. The electrolytes with chloride additions contained 10^{-5}, 10^{-3}, and 10^{-1} N Cl^-.

(a) Potassium Hydroxide Solutions. The anodic dissolution was observed in solutions of unit ionic strength (pH = 13.6). The current density was varied from 0.0002 to 0.1 $amp \cdot cm^{-2}$. The data are shown in Tables V and VIII, Appendix D. The apparent valence was approximately six. A qualitative determination(13) of the molybdenum species in solution was made by acidifying the electrolyte with HCl and then reducing it with $SnCl_2$. A blue color developed which was attributed to "molybdenum blue," a mixture of Mo(V) and Mo(VI). The absence of a pronounced red color initially signified that no Mo(VII) was present. This indicated that the species in solution were Mo(VI) which exist as $MoO_4^=$. Brown-colored particles of a near colloidal nature came off the anode over the entire range of current density. Very thick dark films were also observed on the anode surface. Photomicrographs of the corroded surface are shown in Figure 3. Table I shows the x-ray diffraction data from the film formed on the molybdenum surface at a current density of 0.001 amp·cm^{-2}. No pitting was noted and there was no noticeable effect of chloride ions. Plots of the variation of apparent valence with current density are shown in Figure 6a.

(b) Potassium Carbonate Solutions. The anodic dissolution in 0.667 N K_2CO_3 (unit ionic strength) was carried out at current densities ranging from 0.001 to 0.1 amp·cm^{-2}. The data from these experiments are shown in Tables VI and IX, Appendix D. Figure 6b shows a plot of the apparent valence versus current density. The apparent valence was approximately six and did not vary appreciably with current density. Dark films were again formed on the metal surface during the dissolution, but the electrolyte remained clear and colorless. The pH of the electrolyte remained unchanged at 11.5 during electrolysis. A slight

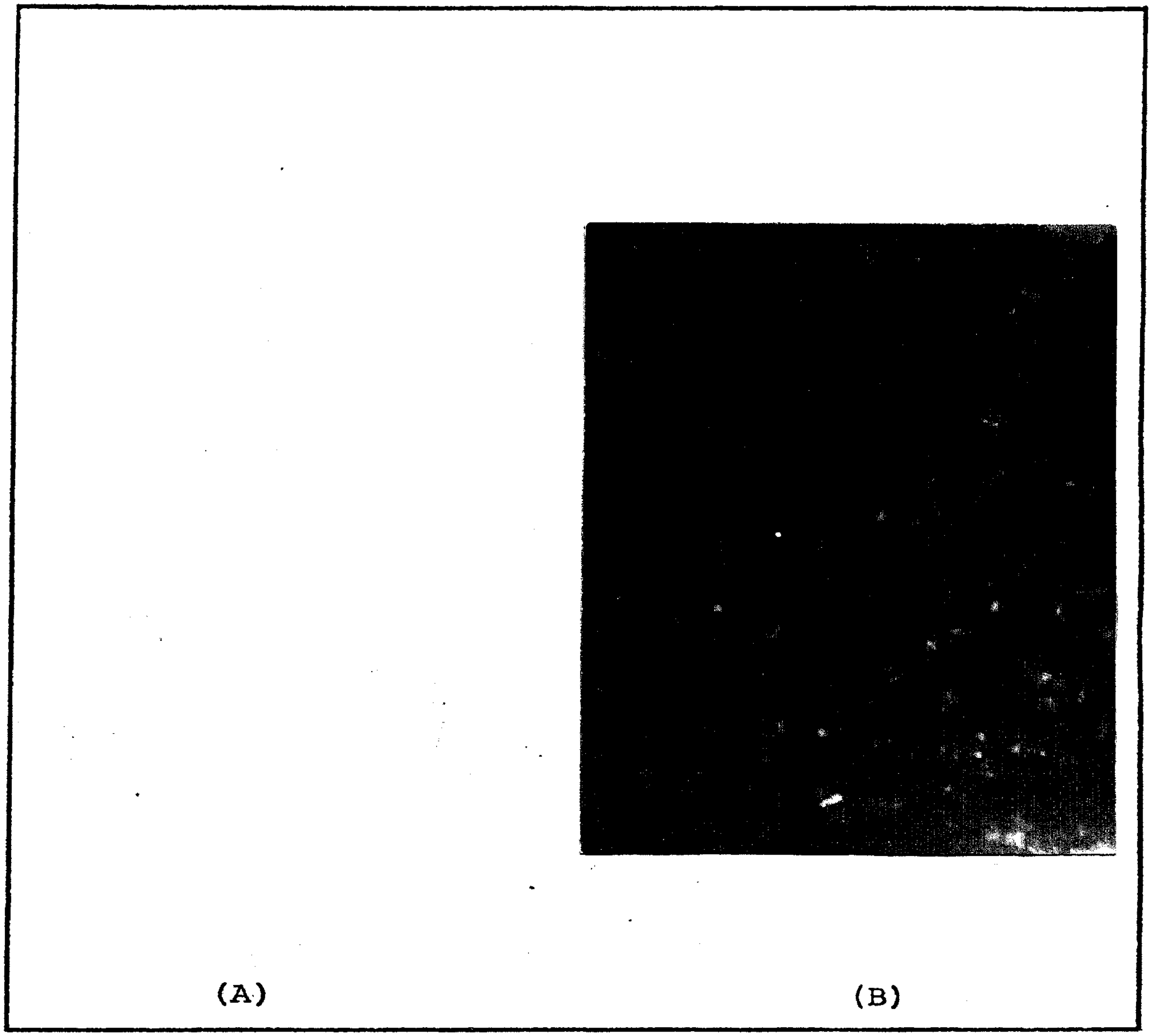

Figure 3. Molybdenum surface (250x) after anodic dissolution for 25 hrs at a current density of 10^{-3} amp$\cdot$cm^{-2} in 1 N KOH solution: (A) Before removal of surface film, (B) After removal of surface film.

TABLE I

LINES OF PATTERN OF ANODIC FILM IDENTIFIED AS γ -PHASE MOLYBDENUM OXIDE*

Measured, θ	d Calc. (Å)	d** (Å)
11.00°	4.05	4.00
17.00°	2.63	2.67
23.70°	1.92	1.94
26.32°	1.74	1.74

Radiation: Cu, λ= 1.542 Å (Powder camera)

*Galvanostatic run at 0.001 amp·cm^{-2} in 1 N KOH for 25 hours. Portions of the film were scraped from the electrode for analysis.

**Pozdeeva, et. al., Corrosion 6, 153 (1966).

gas evolution was observed at the anode at current densities above 0.01 $\text{amp}\cdot\text{cm}^{-2}$. Again, there was no pronounced chloride ion effect. Photomicrographs of an electrode polarized at 0.001 $\text{amp}\cdot\text{cm}^{-2}$ are shown in Figure 4.

(c) Potassium Carbonate-Potassium Sulfate Solutions. The anodic dissolution in $K_2CO_3 + K_2SO_4$ solutions (pH = 9.5) was investigated at current densities ranging from 0.001 to 0.1 $\text{amp}\cdot\text{cm}^{-2}$. The data are shown in Tables VII and X, Appendix D. The apparent valences were again approximately six (see Figure 6c). A dark (almost black) film was formed on the anode. The electrolyte remained clear and colorless. Its pH changed from 9.5 to 4.5 during the course of the run. As observed in the other solutions, there was no pronounced chloride ion effect. Table II shows the x-ray diffraction data from the film formed on the molybdenum surface at a current density of 0.003 $\text{amp}\cdot\text{cm}^{-2}$ with a chloride ion addition of 10^{-1}. A photomicrograph of the corroded surface is shown in Figure 5.

4. Sample Calculations. The method of calculating the apparent valence was the same for all solutions. The data from the anodic dissolution in 1 N KOH (Table V) have been used for the following illustration.

The theoretical weight-loss of molybdenum was calculated using Faraday's law:

$$w_a = \frac{ItA}{nF} \tag{14}$$

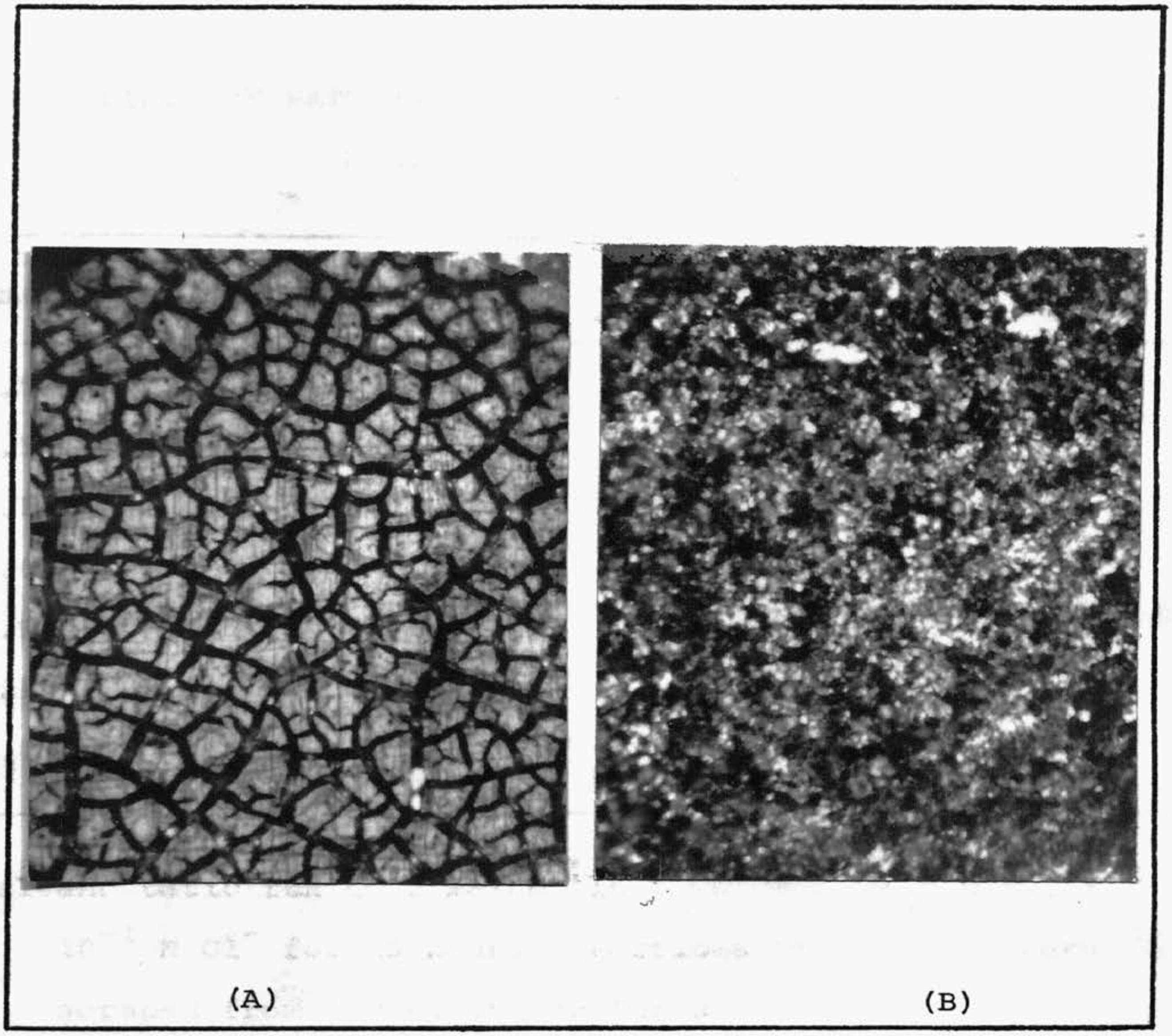

Figure 4. Molybdenum surface (250x) after anodic dissolution for 25 hrs at a current density of 10^{-3} amp·cm^{-2} in 0.667 N K_2CO_3 solution: (A) Before removal of surface film, (B) After removal of surface film.

TABLE II

LINES OF PATTERN OF ANODIC FILM IDENTIFIED AS MOLYBDENUM TRIOXIDE*

Measured, θ	d Calc. (Å)	d A.S.T.M. (Å)
13.50	3.28	3.26
14.55	3.07	3.06
16.75	2.68	2.65
18.65	2.40	2.33
20.90	2.16	2.13
23.15	1.96	1.96
24.00	1.64	1.63

*Galvanostatic run at 3 $ma \cdot cm^{-2}$ in K_2CO_3 + 0.666N K_2SO_4 + 10^{-1} N Cl^- for 25 hours. Portions of the film were scraped from the electrode for analysis.

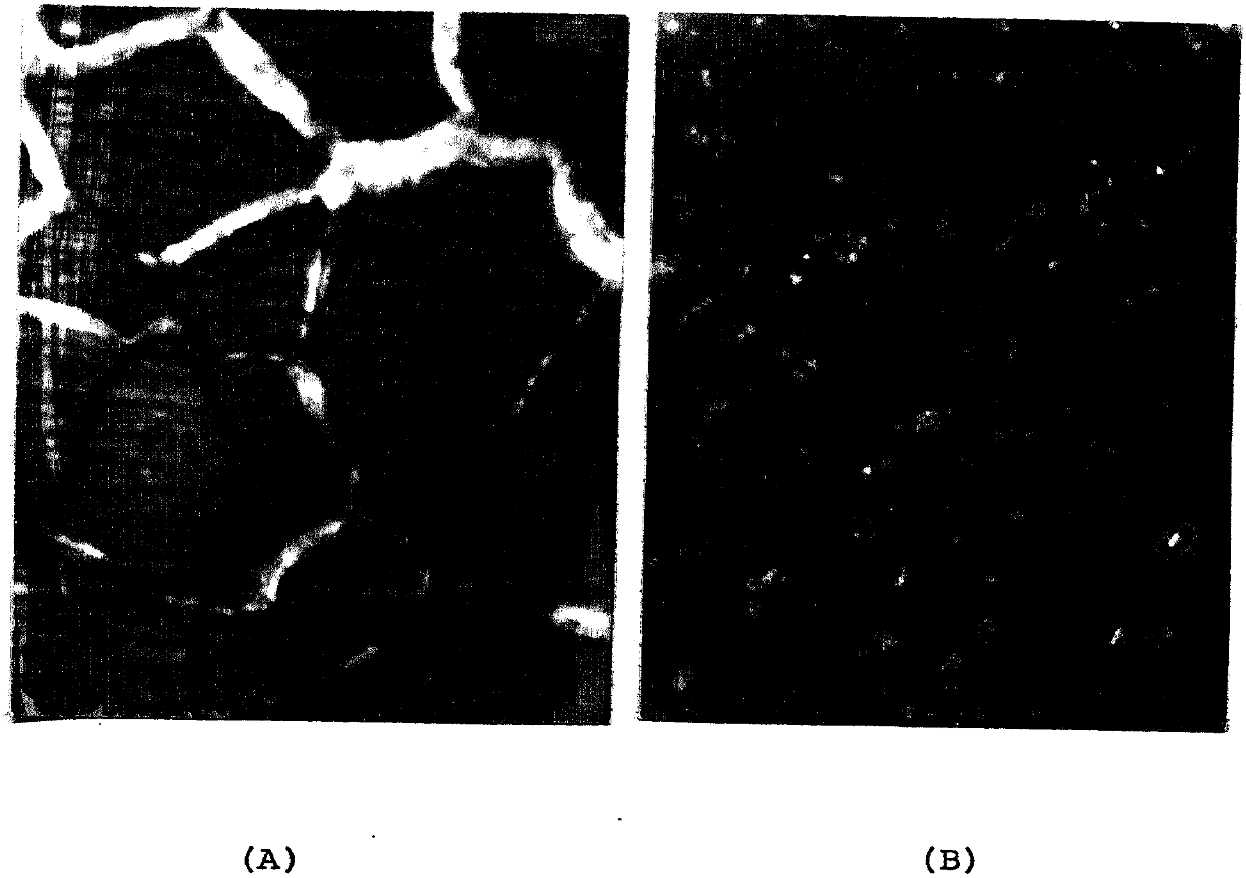

Figure 5. Molybdenum surface (250x) after anodic dissolution for 25 hrs at a current density of 10^{-3} $amp \cdot cm^{-2}$ in 0.001 N K_2CO_3 + 0.666 N K_2SO_4 solution: (A) Before removal of surface film, (B) After removal of surface film.

$$= \frac{(0.0314)(88{,}776)(95.95)}{(96{,}486)\ (6)}$$

$$= 0.0462 \text{ gm}$$

The apparent valence Z_i was calculated using the equation

$$Z_i = \frac{(\text{theoretical weight-loss})\ (\text{normal valence})}{(\text{experimental weight-loss})} \tag{15}$$

$$= \frac{(0.04620)\ (6)}{(0.04627)}$$

$$= 5.99$$

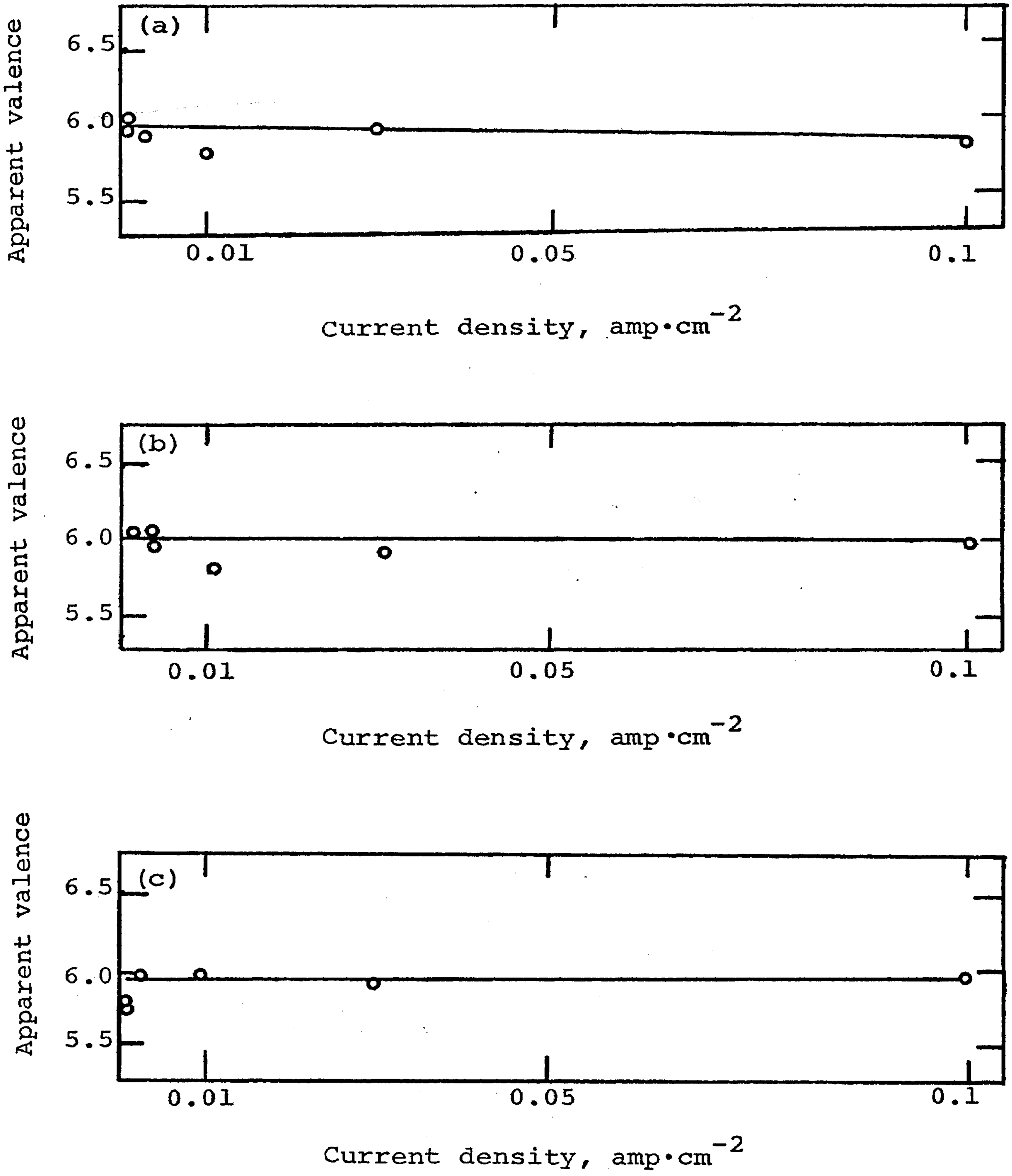

Figure 6. Effect of current density on the apparent valence of molybdenum during anodic dissolution in (a) 1 N KOH, (b) 0.667 N K_2CO_3 and (c) 0.001 N K_2CO_3 + 0.666 N K_2SO_4.

B. The Current Density-Potential Relationship for the Anodic Dissolution of Molybdenum in Alkaline Solutions.

1. Apparatus. The apparatus for this portion of the investigation is shown in Figure 7. A diagram of the teflon holder used in these studies is shown in Figure 8. The temperature was controlled at 25 ± 0.1°C. A calomel (1 N KCl) reference electrode was connected to the anode through a Luggin capillary and a salt bridge. A high impedence electrometer was used to measure the potential difference between the anode and the reference electrode. During polarization, the potential difference was maintained at a constant value 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). Similar measurements were then made at increasingly higher potentials.

3. Data and Results. Polarization studies were made in the same electrolytes as the apparent valence measurements. All the potentials are referred to the normal hydrogen electrode (SHE). A summary of the experimental

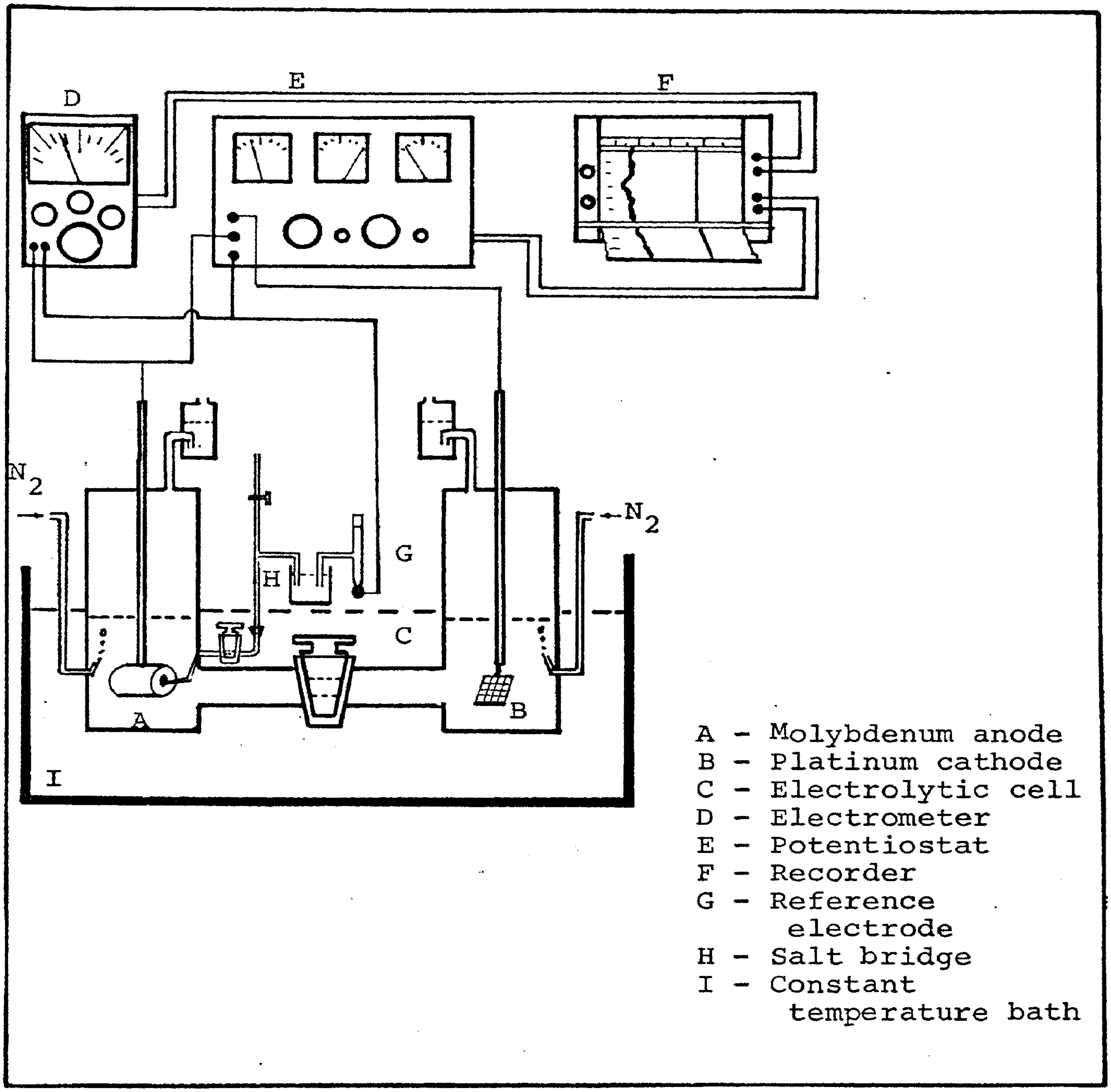

Figure 7. Schematic diagram of the apparatus for polarization studies of the anodic dissolution of molybdenum.

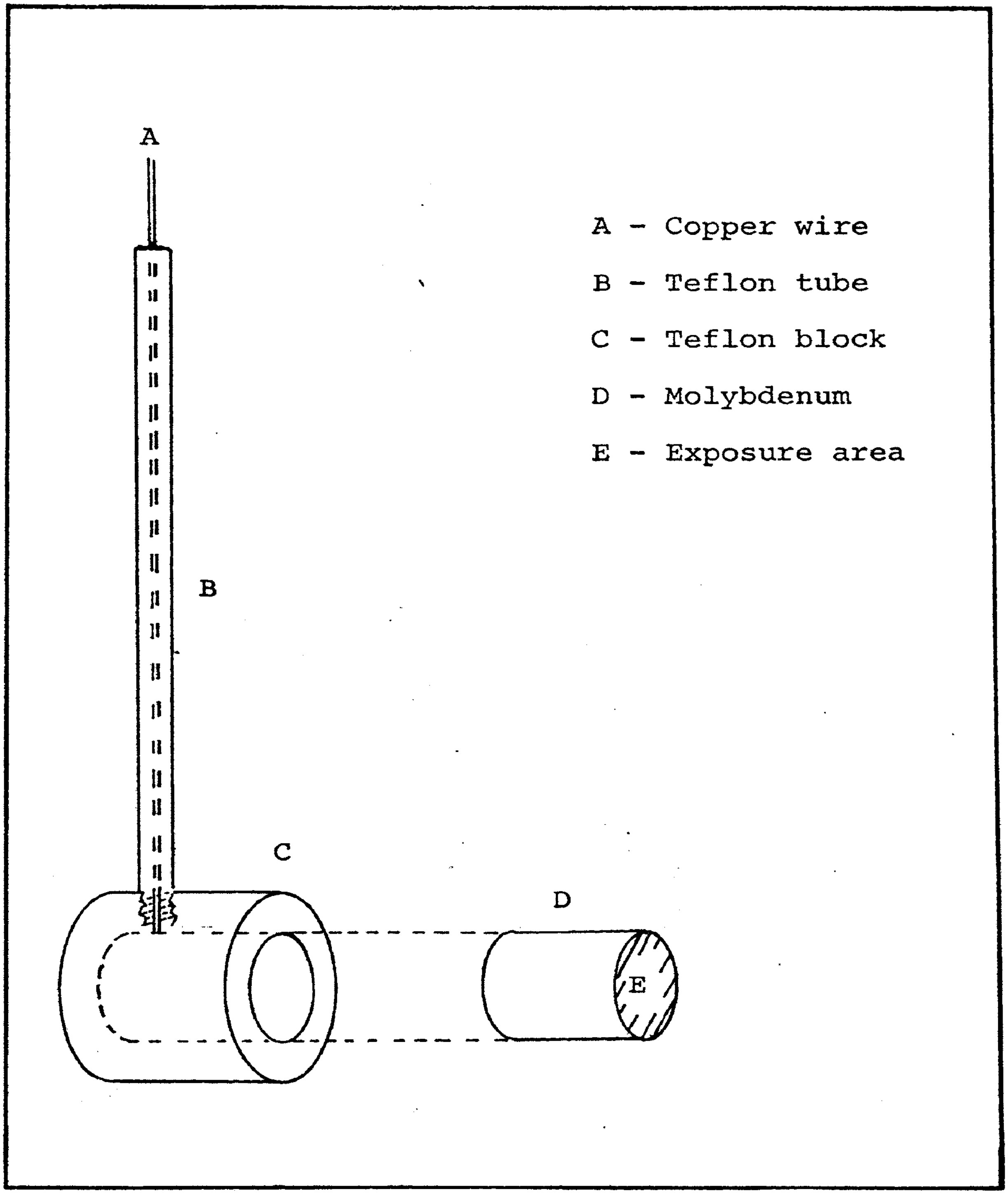

Figure 8. Diagram of the teflon holder for polarization studies of the molybdenum anode.

results follows:

(a) Potassium Hydroxide Solutions. The results of the 1 N KOH, with and without chloride ion additions, are shown in Tables XI to XV, Appendix D. The data from additional runs in 0.1 N KOH are also included in this group and are shown in Tables XVI and XVII. Tafel plots are shown in Figures 9 through 13. The rest potentials of the Mo electrode varied from -0.36 to -0.38 volts (SHE). Limiting currents of approximately 0.40 amp·cm^{-2} were reached. For potentiostatic operation, the highest potential that could be attained was 0.4 volts. No gas evolution was observed under these conditions. Linear Tafel regions over 1.5 - 2.0 decades of current were observed. The slopes and rest potentials have been tabulated in Table IV. An unsteady region (V= -0.2 to -0.15 volts) was observed where the current increased with time, never reaching a steady state. The Tafel slope here appears to be lower than in the steady region.

Galvanostatic techniques using a high voltage power supply were used to polarize the Mo anode to higher potentials in the KOH solution. The results are shown in Table XVIII, Appendix D, and Figure 14. Under these conditions (constant current), the surface film on the anode appeared to thicken and was accompanied by a continual increase of the anode potential. When the potential reached about 90 volts, a slight gas evolution was observed, and the surface film appeared to be stripped from the electrode by the bubble formation. As the film became detached from electrode and fell into the electrolyte, the potential immediately dropped to about 0.9 volts. Continued polarization caused this cycle to be repeated. The electrolyte became blue in color during these experiments. The results of x-ray analysis of the detached films are shown in Table III.

(b) Potassium Carbonate Solutions. Data from these studies are shown in Tables XIX to XXII, Appendix D. Polarization curves are shown in Figures 9 to 12. The rest potential in these electrolytes varied from -0.19 to -0.29 volts. There was no noticeable effect of chloride ion on the polarization behavior.

(c) Potassium Carbonate-Potassium Sulfate Solutions. These data are shown in Tables XXIII to XXVI, Appendix D. Potential-current density plots are shown in Figures 9 to 12. A small pseudo passivation region was found for chloride ion concentrations of 10^{-3} and 10^{-1} N. The rest potentials in these electrolytes were in the region -0.12 to -0.14 volts. A significant change in pH (9.5 to 4.5) occurred during the polarization period.

4. Sample Calculations. The method for calculating the potential is illustrated below. Data from Table XI, Appendix D, have been used for the illustration.

$$V = V_r - V_m \tag{16}$$

TABLE III

LINES OF PATTERN OF ANODIC FILM IDENTIFIED AS β – PHASE MOLYBDENUM OXIDE*

Measured	d Calc. (Å)	d** (Å)
36.05°	1.31	1.36
29.20°	1.58	1.59
20.15°	2.25	2.28
10.75°	4.08	4.03

Radiation: Cu, $\lambda = 1.542$ Å

*Galvanostatic run at 42 $\text{ma}\cdot\text{cm}^{-2}$ in 1 N KOH solution. Portions of film spalled from the surface were collected for analysis.

**Pozdeeva, et. al., Corrosion <u>6</u>, 153 (1966).

where

V = potential of Mo electrode, volts (SHE)

V_r = potential of calomel (1 N KCl) electrode = 0.28 V

V_m = potential read from the electrometer

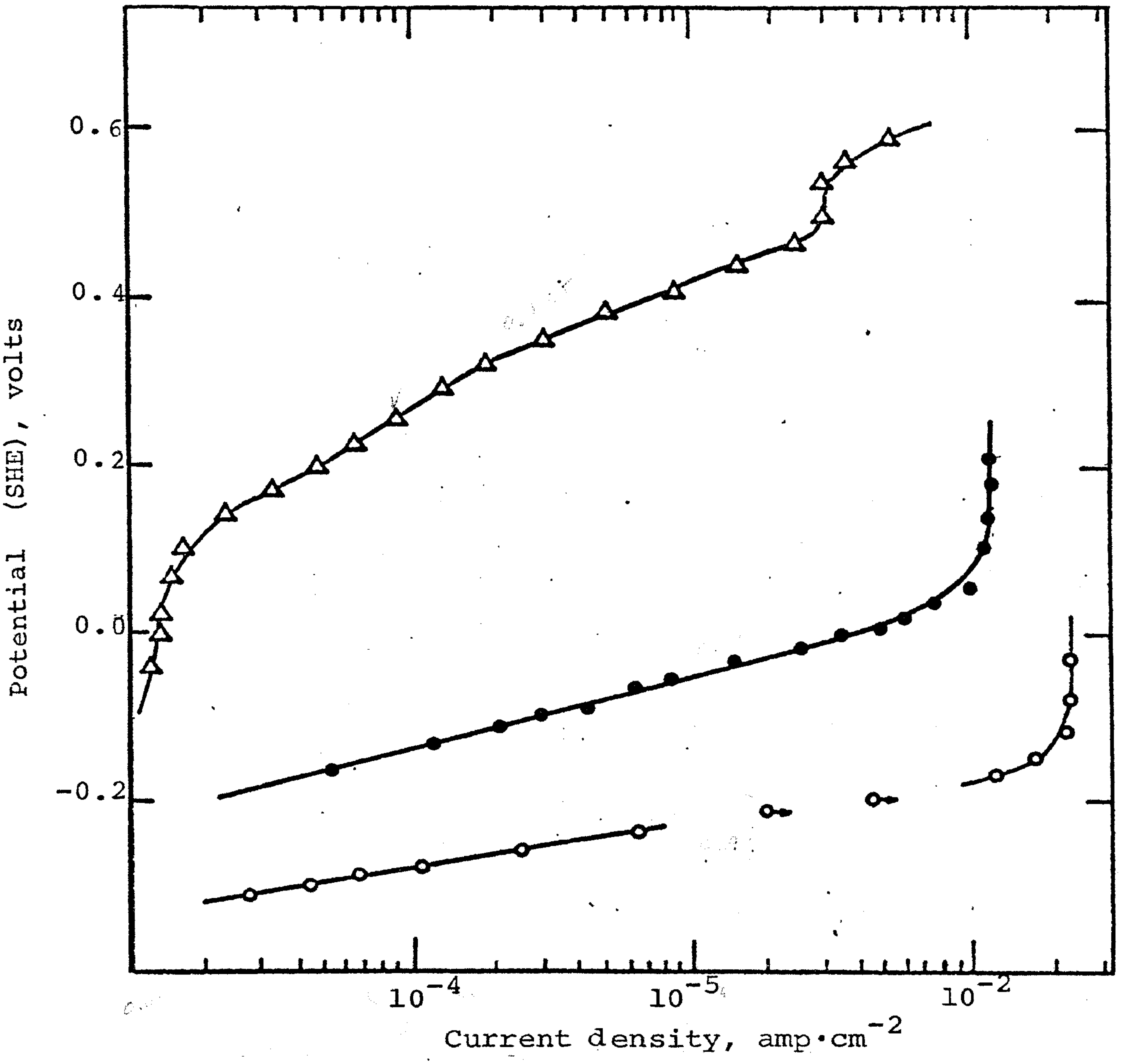

Figure 9. Tafel curves for the anodic dissolution of molybdenum at 25°C. (o, 1 N KOH; ●, 0.667 N K_2CO_3; Δ, 0.001 N K_2CO_3 + 0.666 N K_2SO_4; o→ , unsteady state)

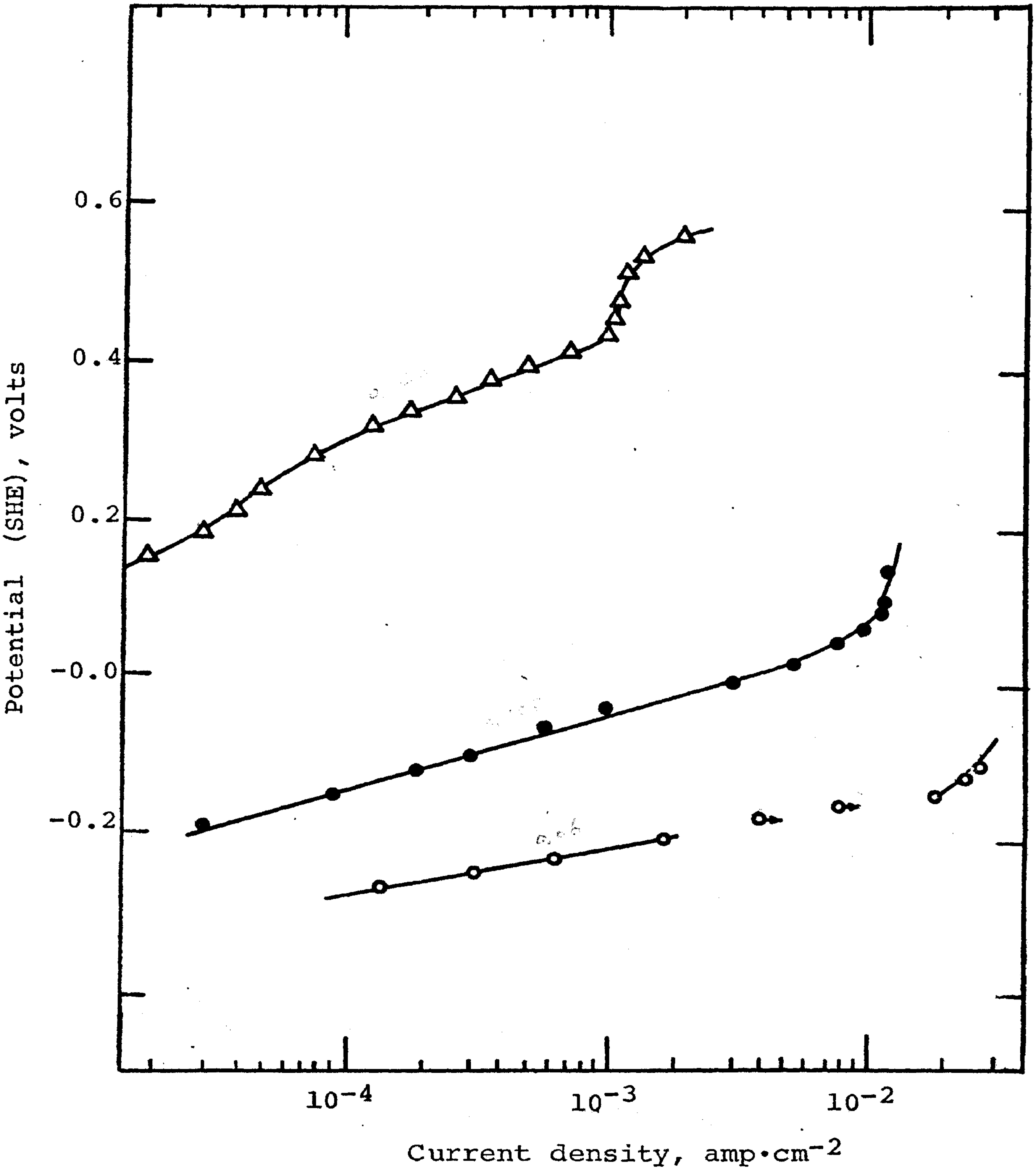

Figure 10. Tafel curves for the anodic dissolution of molybdenum at 25°C. (o, 1 N KOH + 10^{-5} N Cl^-; ●, 0.667 N K_2CO_3 + 10^{-5} N Cl^-; Δ, 0.001 N K_2CO_3 + 0.666 N K_2SO_4 + 10^{-5} N Cl^-; o→, unsteady state.)

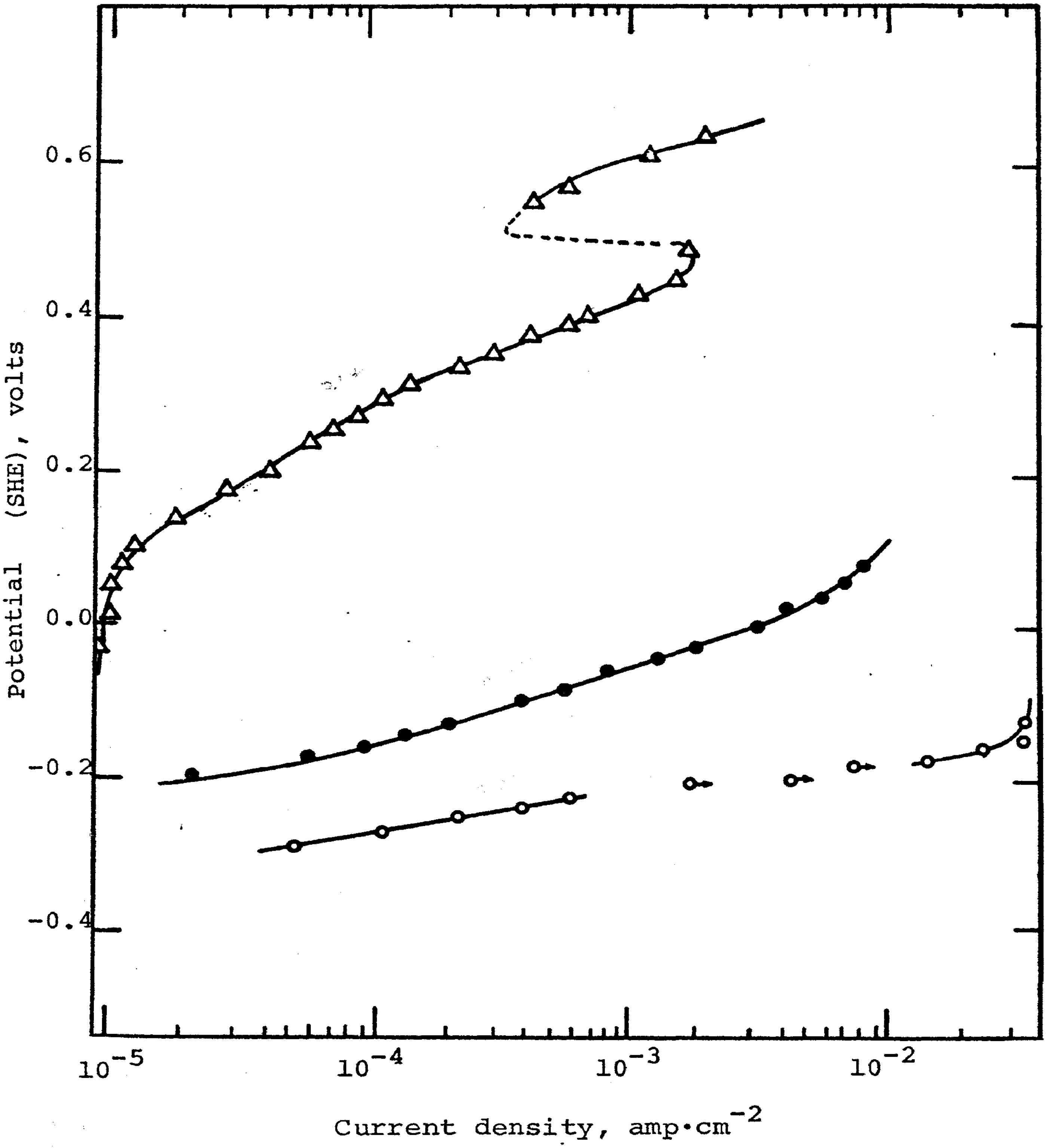

Figure 11. Tafel curves for the anodic dissolution of molybdenum at 25°C. (o, 1 N KOH + 10^{-3} N Cl$^-$; ●, 0.667 N K_2CO_3 + 10^{-3} N Cl$^-$; Δ, 0.001 N K_2CO_3+ 0.666 N K_2SO_4 + 10^{-3} N Cl$^-$; o→, unsteady state)

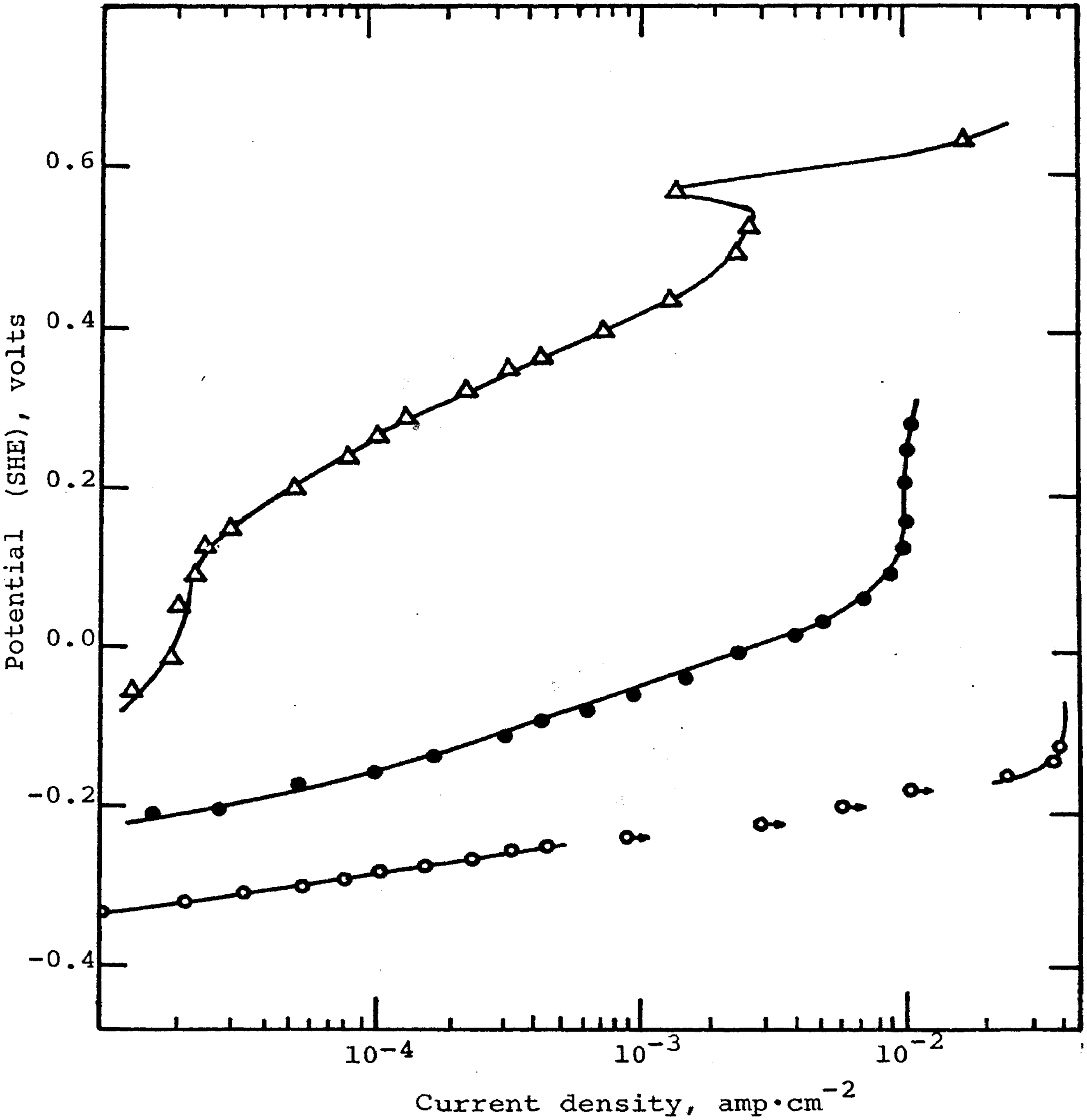

Figure 12. Tafel curves for the anodic dissolution of molybdenum at 25°C. (o, 1 N KOH + 10^{-1} N Cl^-; ●, 0.667 N K_2CO_3 + 10^{-1} N Cl^-; Δ, 0.001 N K_2CO_3 + 0.666 N K_2SO_4 + 10^{-1} N Cl^-; o→, unsteady state)

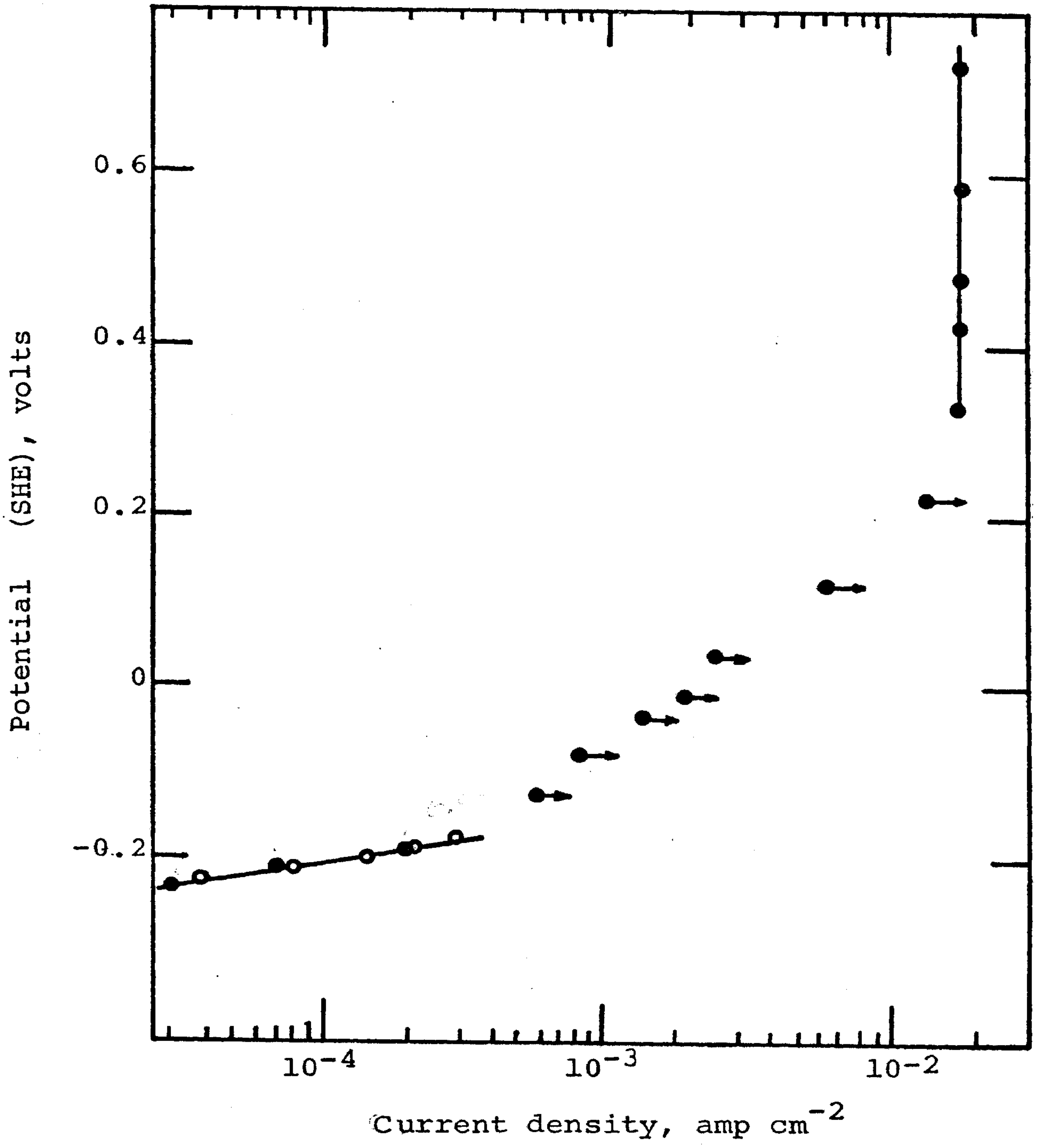

Figure 13. Tafel curves for the anodic dissolution of molybdenum in 0.1 N KOH at 25°C (o, run 1; ●, run 2; ●→, unsteady state)

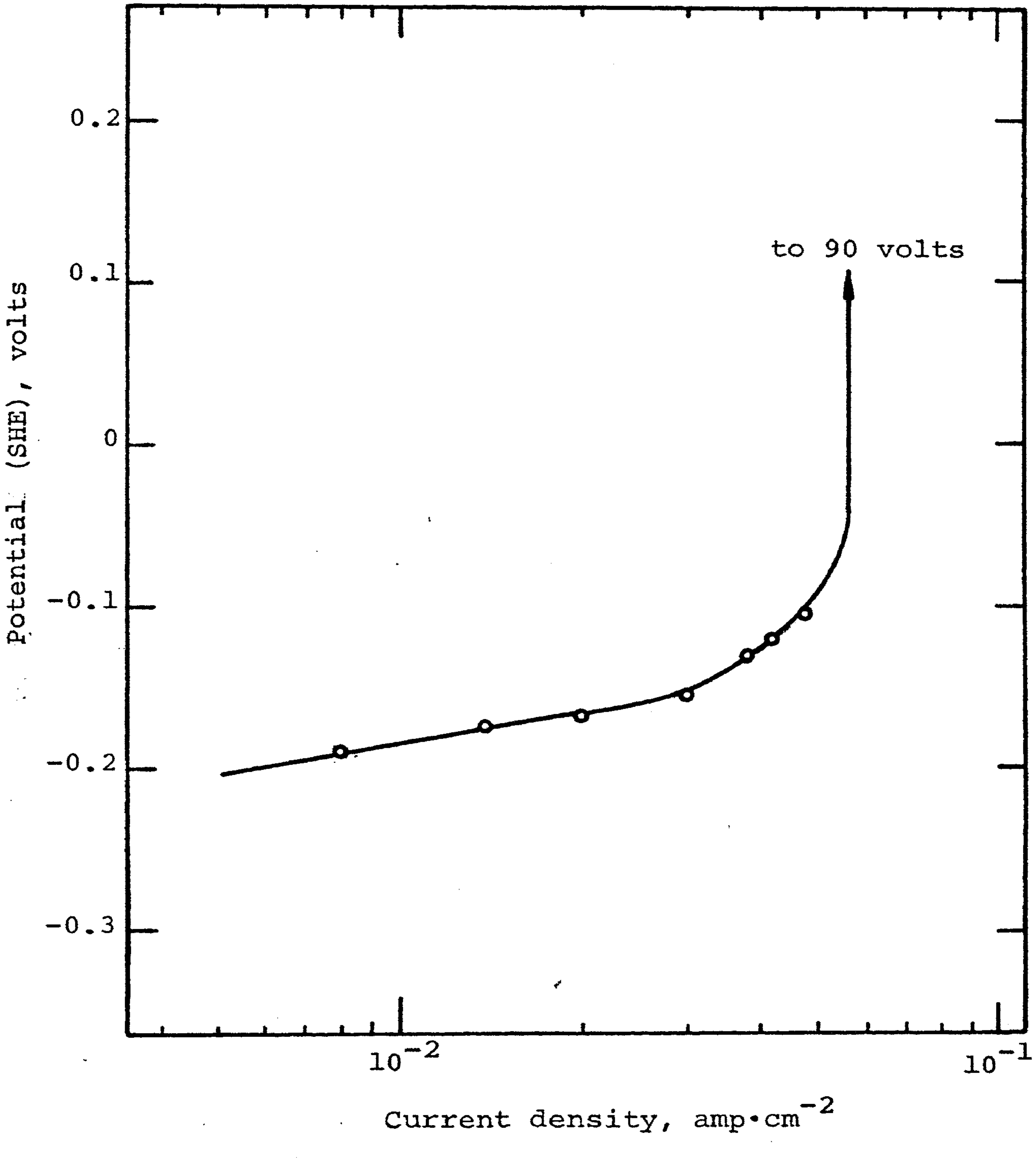

Figure 14. Tafel curves (galvanostatic studies) for the anodic dissolution of molybdenum in 1 N KOH at 25°C.

TABLE IV

REST POTENTIAL AND TAFEL SLOPE OF MOLYBDENUM IN DIFFERENT ELECTROLYTES AT 25°C

Electrolytes	pH	Rest Potential (volts)	Tafel Slope (volts)
1 N KOH	13.6	-0.370	0.060
0.1 N KOH	12.7	-0.260	0.060
0.667 N K_2CO_3	11.5	-0.262	0.110
0.001 N K_2CO_3+ 0.666 N K_2SO_4	9.5*	-0.138	0.135
1 N KOH + 10^{-5} N Cl^-	13.6	-0.370	0.060
0.667 N K_2CO_3 + 10^{-5} N Cl^-	11.5	-0.280	0.105
0.001 N K_2CO_3 + 0.666 N K_2SO_4 + 10^{-5} N Cl^-	9.5*	-0.130	0.140
1 N KOH + 10^{-3} N Cl^-	13.6	-0.365	0.058
0.667 N K_2CO_3 + 10^{-3} N Cl^-	11.5	-0.280	0.105
0.001 N K_2CO_3 + 0.666 N K_2SO_4 + 10^{-3} N Cl^-	9.5*	-0.120	0.140
1 N KOH + 10^{-1} N Cl^-	13.6	-0.353	0.059
0.667 N K_2CO_3 + 10^{-1} N Cl^-	11.5	-0.270	0.120
0.001 N K_2CO_3 + 0.666 N K_2SO_4 + 10^{-1} N Cl^-	9.5*	-0.134	0.140

*pH of electrolyte changed from 9.5 to 4.5 during the polarization experiment.

IV. DISCUSSION

The apparent valence of molybdenum determined from these studies can be expressed as follows for $10^{-3} < i < 10^{-1}$ $\text{amp}\cdot\text{cm}^{-2}$:

<u>1 N KOH (pH = 13.6)</u>

$$V_i \ (\pm 0.09) = 5.96 - 0.95\ i \tag{17}$$

<u>0.667 N K_2CO_3 (pH = 11.5)</u>

$$V_i \ (\pm 0.14) = 5.95 + 0.21\ i \tag{18}$$

<u>0.001 N K_2CO_3 + 0.666 N K_2SO_4 (pH = 9.5)</u>

$$V_i \ (\pm 0.18) = 5.95 + 0.58\ i \tag{19}$$

The values are approximately +6 and relatively independent of current density. The resultant ions in solution were identified as $MoO_4^{=}$. These indicate all electron transfer processes to be occurring on the anode and that the overall reaction is:

$$Mo(s) + 3\ OH^-(aq) + H_2O(aq) = MoO_4^{=}(aq) + 5\ H^+(aq) + 6\ e \tag{20}$$

or $$Mo(s) + 4\ OH^-(aq) = MoO_4^{=}(aq) + 4\ H^+(aq) + 6\ e \tag{21}$$

The measured rest potentials vs. pH are shown in Figure 15, along with the standard values (E^o) for several other possible reactions. When the pH effects are taken into account, almost all reactions are eliminated as being responsible for the rest potentials with the exceptions of:

$$Mo_2O_5(s) + OH^-(aq) + 2\ H_2O(aq) = 2\ H_2MoO_4(s) + H^+ + 2\ e \tag{22}$$

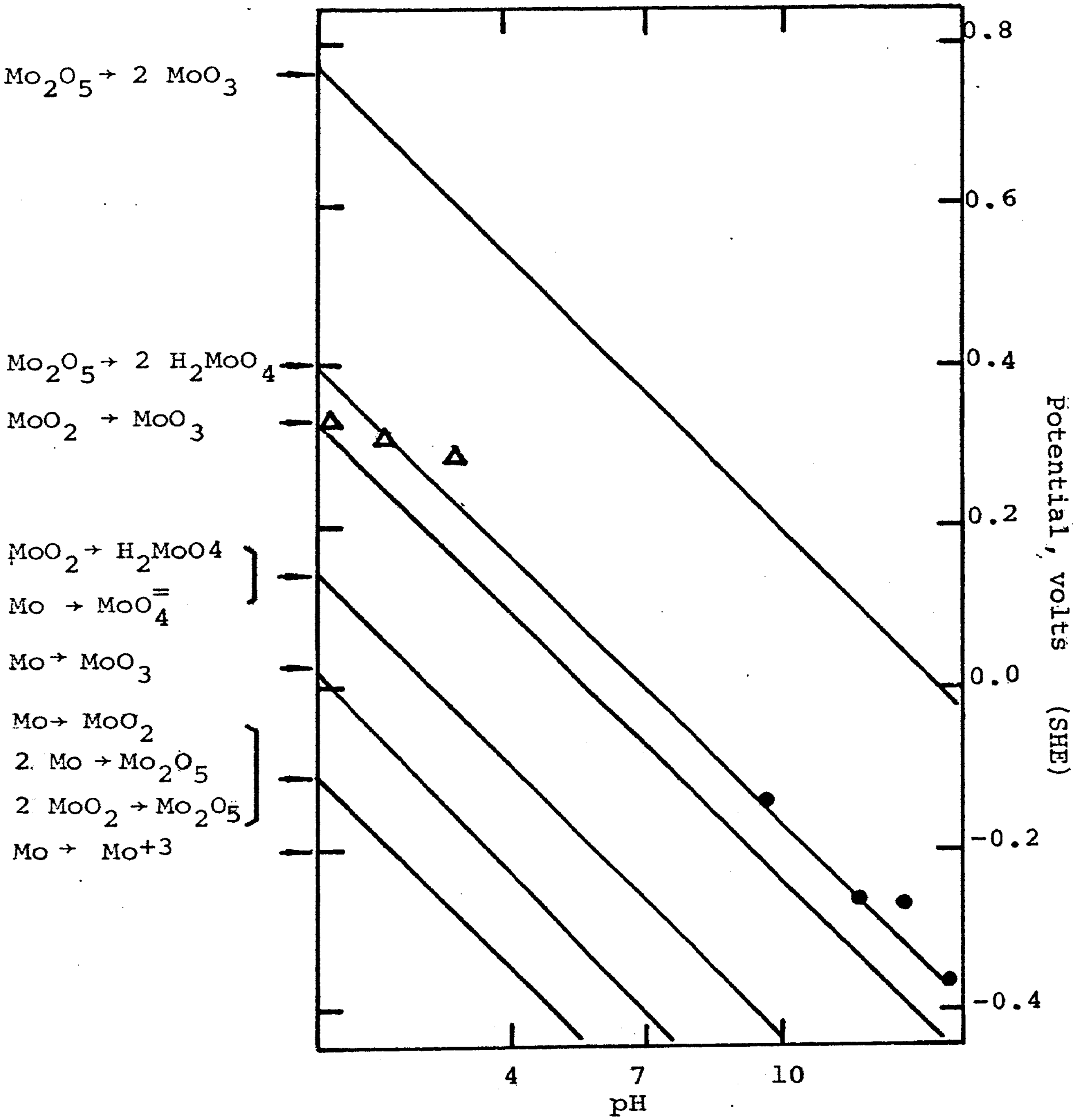

Figure 15. Observed rest potentials of the molybdenum anode compared with standard potentials of molybdenum and several molybdenum compounds at 25°C. (●, data from Table IV, Δ , data observed by Chen (15))

or $$MoO_2(s) + H_2O(aq) = MoO_3 + 2\ H^+ + 2\ e \qquad (23)$$

Due to the tendency of MoO_3 to hydrolyse in water, it appears that the equilibrium surface reaction will be more closely represented by equation (22) than by equation (23). This is also supported by the diffuseness of the lines in the x-ray patterns which indicate an amorphous nature of the film that is more easily attributed to H_2MoO_4 than to MoO_3. When no external potential is applied and at low current density, the surface film is predominantly the highly conductive γ-phase oxide ($MoO_{2.65}$-$MoO_{2.75}$). At higher current density, the film thickens by accumulation of the β-phase ($MoO_{2.89}$) which is probably characterized by the oxide Mo_4O_{11}. The rest potentials measured in the acid region also add support to this mechanism (see Figure 15).

Considering the initial formation of Mo_2O_5 to be very rapid and the electrode surface to have a high coverage of this species (or some of its subsequent oxidation products), the initial part of the overall dissolution mechanism will not affect the observed kinetic parameters. This can be expressed by the overall reaction for the formation of Mo_2O_5,

$$2\ Mo(s) + 5\ OH^-(aq) = Mo_2O_5(s) + 5\ H^+(aq) + 10\ e \qquad (24)$$

The observed kinetic parameters are thus associated with the portion of the mechanism in which Mo_2O_5 is further oxidized and ultimately ends up in solution as $MoO_4^=$ ions. All the experimental observations can be explained by the following sequence if, in addition to the usual assumptions and approximations, one assumes that the specific rates of each of the reactions do not differ greatly:

$$Mo_2O_5(s) + OH^-(aq) = Mo_2O_5OH(s) + e \qquad (25)$$

$$Mo_2O_5OH(s) + Mo_2O_5(s) = Mo_4O_{10}OH(s) \qquad (26)$$

$$Mo_4O_{10}OH(s) = Mo_4O_{11}(s) + H^+(aq) + e \qquad (27)$$

$$Mo_4O_{11}(s) = 2\ MoO_3(s) + Mo_2O_5(s) \qquad (28)$$

$$MoO_3(s) + H_2O(aq) = H_2MoO_4(s) \qquad (29)$$

$$H_2MoO_4(s) + 2\ OH^-(aq) = MoO_4^=(aq) + 2\ H_2O(aq) \qquad (30)$$

For the dissolution in KOH, a Tafel slope of 60 mv was observed (see Table IV). This would be associated with equation (26) in the above sequence being rate determining. The expression for the current assuming equation (25) to be in quasi-equilibrium is

$$i = F\ k_{26}\ \theta_{Mo_2O_5OH}\ \theta_{Mo_2O_5} \qquad (31)$$

where

$$\theta_{Mo_2O_5OH} = K_{25}\ \theta_{Mo_2O_5}\ a_{OH^-}\ \exp(FV/RT) \qquad (32)$$

For $\theta_{Mo_2O_5} \cong 1$

$$i = F\ k_{26}K_{25}\ a_{OH^-}\ \exp(FV/RT) \qquad (33)$$

$$\left(\frac{\partial V}{\partial \log i}\right) = \frac{2.303\ RT}{F} = 0.059 \text{ volts} \qquad (34)$$

It should be noted that the first order pH dependence as shown in equation (33) was also observed experimentally (see Figure 16). The unsteady region (V = -0.2 to -0.15

volts) where the current increased with time and the Tafel slope appears to be lowered would be associated with a shift in the r.d.s. from equation (26) to either equation (27), (28), or (29). As the potential is increased, $Mo_4O_{10}OH$, Mo_4O_{11}, and MoO_3 accumulate on the surface. If one of these accumulates faster than it is being removed, the r.d.s. may be shifted to the second electron transfer or some chemical step following it. This will lower the Tafel slope to 40 mv (second electron transfer r.d.s.) or 30 mv(a chemical r.d.s. following the second electron transfer). The expression for the current with equation (27) as the r.d.s. is

$$i = F\, k_{27}\, K_{25}\, K_{26}\, \theta_{Mo_2O_5}\, a_{OH^-}\, \exp\left(\frac{(2-\alpha)FV}{RT}\right) \qquad (35)$$

$$\left(\frac{\partial V}{\partial \log i}\right) = 2.303\ RT/(2-\alpha)F = 0.040 \text{ volts} \qquad (36)$$

The expressions for the current with equation (28) or (29) rate determining are

$$i = F\, k_{28}\, K_{25}\, K_{26}\, K_{27}\, (\theta_{Mo_2O_5})^2\, a_{OH^-}\, \exp\left(\frac{2\ FV}{RT}\right) \qquad (37)$$

or

$$i = F\, k_{29}\, K_{25}\, K_{26}\, K_{27}\, K_{28}\, (\theta_{Mo_2O_5})^2\, a_{OH^-}\, \exp\left(\frac{2FV}{RT}\right) \qquad (38)$$

Both equations (37) and (38) have the same Tafel slope, i.e.,

$$\left(\frac{\partial V}{\partial \log i}\right) = 2.303\ RT/2F = 0.030 \text{ volts} \qquad (39)$$

The change in Tafel slope to 120 mv in K_2CO_3 solution (pH = 11.5) is explained by the decreased OH^- concentration which causes equation (25) to become rate determining.

$$i = F\, k_{25}\, \theta_{Mo_2O_5}\, a_{OH^-}\, \exp\left(\frac{(1-\alpha)FV}{RT}\right) \qquad (40)$$

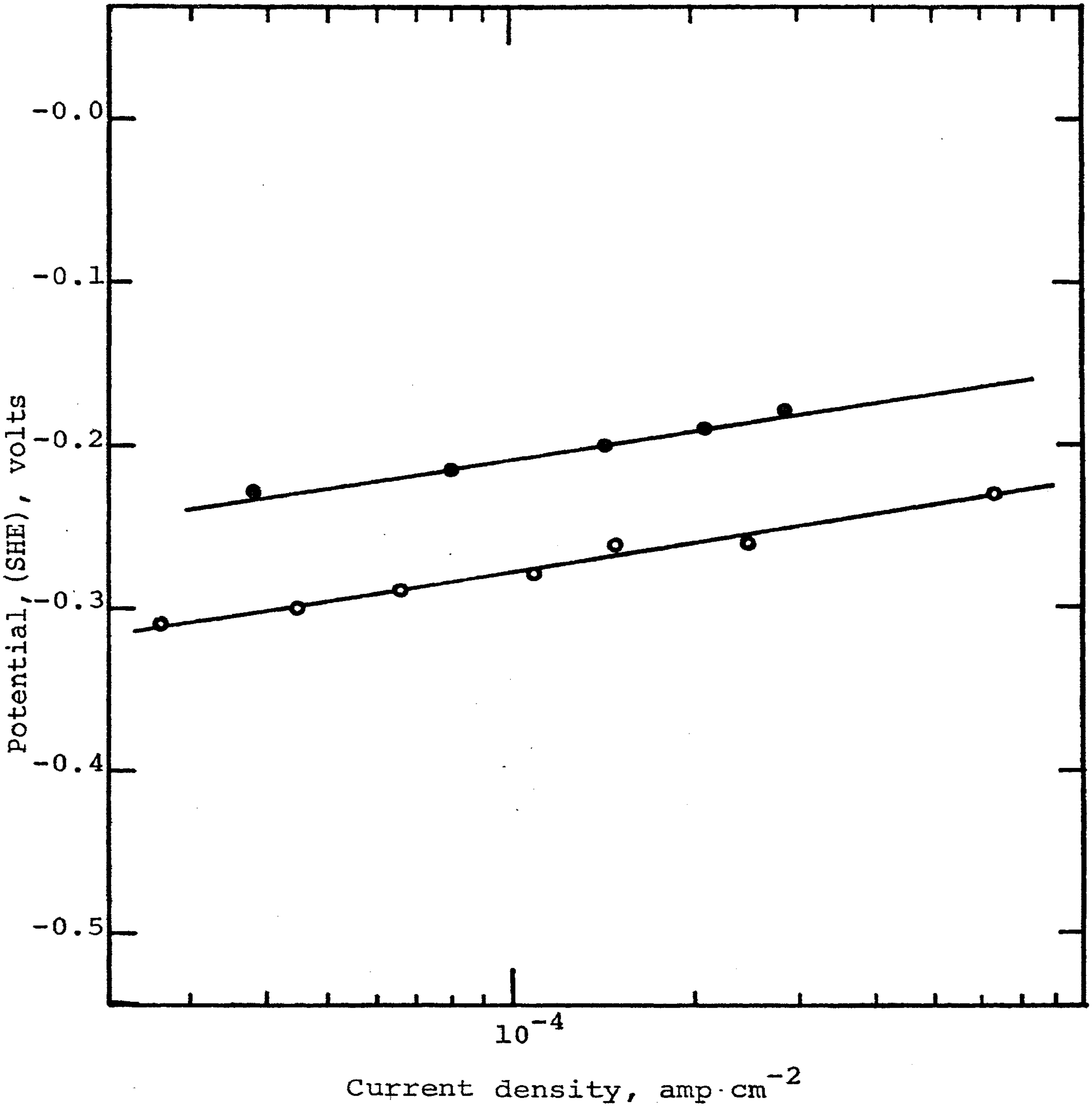

Figure 16. Effect of pH on the anodic dissolution of molybdenum in 0.1 N and 1.0 N KOH at 25°C.

$$\left(\frac{\partial V}{\partial \log i}\right) = \frac{2.303\ RT}{(1 - \alpha)F} = 0.118 \text{ volts} \qquad (42)$$

The limiting currents found on Mo (see Figures 9 to 14) can arise from two different factors. One is the diffusion of OH^- to the electrode as shown in equation (25). This explanation was offered by Eidman$^{(12)}$ as a result of his studies. However, if this were the case, either water could substitute for OH^- at a somewhat higher potential, or oxygen would be evolved from the highly conductive Mo_2O_5 surface at potentials not greater than a few volts. Since oxygen is not evolved at potentials up to 90 volts, it appears that there is another reason for the limiting currents, namely the accumulation and covering of the surface by the highly nonconducting MoO_3 or the hydrated oxide H_2MoO_4. Thus, the current in this potential region becomes a function of the dissolution rate of the unstable MoO_3 which in turn is pH dependent$^{(14)}$. This also explains the absence of oxygen evolution in that most all the potential drop between the electrode and solution would take place across the nonconductive MoO_3 film so that a sufficient potential to evolve oxygen is never realized on the surface. This is substantiated to some extent by comparing the experimentally observed limiting current with those calculated assuming diffusion control. Potter$^{(16)}$ gives the equations as:

For stirred solutions,

$$i = 7.2 \times 10^{-1} z a_i \tag{42}$$

For unstirred solutions,

$$i = 1.4 \times 10^{-2} z a_i \tag{43}$$

For $z = 6$ and unit activity of the OH^-, the diffusion limited currents are $0.084 < i < 4.2$ amp·cm^{-2}. These calculated values are considerably larger than the observed ones, thus implying the observed values are not diffusion limited.

The absence of a Cl^- effect is seen by observing the apparent valence, rest potentials, and Tafel slopes with and without it present. No significant changes are noted.

V. RECOMMENDATIONS

It is recommended that valence studies under the present experimental conditions be made by using neutral electrolytes. Nitrate ions would be of special interest as they may cause passivation at higher concentrations.

Studies of the anodic behavior in the presence of a significant molybdenum ion concentration might be of interest also.

VI. APPENDICES

Appendix A

Materials

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

1. Potassium Hydroxide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

2. Potassium Carbonate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

3. Potassium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

4. Potassium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

5. Mercurous Chloride. Reagent grade, meets ACS specifications. Merck and Company, Inc., Rahway, N.J.

6. Nitrogen. Prepurified grade. Matheson Co., Joliet, Ill.

7. Molybdenum. One inch rod, 99.9% purity. Typical impurities (ppm): C 150; O 360; Al <10; Cu <10; Co <10; Cr <10; Cu <10; Fe <10; H <10; N <10; Ni <10. Electronic Space Products, Inc., Los Angeles, Calif.

Appendix B

Equipment

1. Surface Preparation of Molybdenum Specimens

a. Belt Surfacer. Buehler No. 1250, Buehler Ltd., Evanston, Ill.

b. Hand Grinder. Handimet, 4 stages (grit 240 to 600), Buehler No. 1470, Buehler Ltd., Evanston, Ill.

2. Electrolysis and Potential Measurements

a. Power Supply. Model 711A, DC regulated voltage (0 - 500 volts), Hewlett-Packard Co., Loveland, Col.

b. Electrometer. Model 610B, Keithy Instruments, Inc., Cleveland, Ohio.

c. Ammeter. Model 931, Weston Electric Instrument Corp., Newark, N.J.

d. Power Resistor. Model 240-C, Clarostat Mfg. Co., Inc., Dover, N.H.

e. Potential Controller. Model 4100, Continental Oil Co., Anotrol Division, Ponca City, Okla.

Appendix C

Miscellaneous Experimental Procedures

1. Surface Preparation of Molybdenum Procedures. The following procedure was used for the molybdenum metal surface preparation:

a. All pits and irregularities were removed from the metal surface with a wetted belt surfacer equipped with a No. 150 grit abrasive cloth belt.

b. The 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.

c. The sample was rinsed with distilled water.

d. The surface was etched in dilute nitric acid and rinsed again with distilled water.

2. Treatment of Films Formed on the Molybdenum Electrode.

a. The surface was thoroughly rinsed with distilled water.

b. The surface was then massaged with a rubber policeman until the film was loosened.

c. The loosened film was washed off the surface into a beaker with distilled water.

Appendix D

Experimental Data

(Tables V to XXVI)

TABLE V

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 1.0 N KOH AT 25°C (pH = 13.6)

Current Density ($amp \cdot cm^{-2}$)	Time (sec)	Weight-loss of Molybdenum Calc (gm)	Weight-loss of Molybdenum Expt (gm)	Apparent Valence
0.0002*	518,400	0.05397	0.05318	6.09
0.001*	88,776	0.04620	0.04627	5.99
0.001*	81,000	0.04215	0.04179	6.05
0.003*	60,300	0.09414	0.09309	5.94
0.010*	22,175	0.11540	0.11859	5.84
0.010*	19,180	0.09982	0.10176	5.88
0.030*	18,600	0.29040	0.29090	5.99
0.100**	2,500	0.03254	0.03327	5.87
0.100**	3,000	0.03902	0.03955	5.92

TABLE VI

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 0.667 N K_2CO_3 AT 25°C (pH = 11.5)

Current Density ($amp \cdot cm^{-2}$)	Time (sec)	Weight-loss of Molybdenum Calc (bm)	Weight-loss of Molybdenum Expt (gm)	Apparent Valence
0.001*	90,000	0.04684	0.04660	6.03
0.003*	36,060	0.05620	0.05574	6.05
0.003*	36,360	0.05680	0.05725	5.95
0.010*	10,800	0.05623	0.05806	5.81
0.030*	3,600	0.05623	0.05699	5.91
0.100**	1,800	0.02343	0.02345	6.00

* anode area = 3.14 cm^2

** anode area = 0.785 cm^2

TABLE VII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 AT 25°C (pH = 9.5)

Current Density (amp· cm^{-2})	Time (sec)	Weight-loss of Molybdenum Calc (gm)	Weight-loss of Molybdenum Expt (gm)	Apparent Valence
0.001*	110,800	0.05769	0.06002	5.77
0.001*	90,000	0.04686	0.04885	5.70
0.003*	36,000	0.05623	0.05680	5.94
0.010*	10,800	0.05623	0.05678	5.94
0.030*	3,600	0.05623	0.05722	5.90
0.100**	1,800	0.02343	0.02346	5.99

TABLE VIII

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 1.0 N KOH IN THE PRESENCE OF CHLORIDE IONS AT 25°C

Cl^- (N)	c. d. (amp· cm^{-2})	Time (sec)	Weight-loss of Mo Calc (gm)	Weight-loss of Mo Expt (gm)	Apparent Valence
0	0.003	60,300	0.09414	0.09309	5.94
10^{-5}	0.003	36,000	0.05623	0.05602	6.02
10^{-3}	0.003	36,000	0.05623	0.05599	6.00
10^{-1}	0.003	36,000	0.05623	0.05542	6.09
0	0.030	18,600	0.29040	0.29090	5.99
10^{-5}	0.030	3,600	0.05623	0.05726	5.89
10^{-3}	0.030	3,600	0.05623	0.05786	5.83
10^{-1}	0.030	3,600	0.05623	0.05638	5.98

* anode area = 3.14 cm^2

** anode area = 0.785 cm^2

TABLE IX

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 0.667 N K_2CO_3 IN THE PRESENCE OF CHLORIDE IONS AT 25°C

Cl^- (N)	c. d. ($amp \cdot cm^{-2}$)	Time (sec)	Weight-loss of Mo Calc (gm)	Weight-loss of Mo Expt (gm)	Apparent Valence
0	0.003	36,360	0.05680	0.05725	5.95
10^{-5}	0.003	36,000	0.05623	0.05629	5.99
10^{-3}	0.003	36,000	0.05623	0.05662	5.96
10^{-1}	0.003	25,200	0.03936	0.03857	6.12
0	0.030	3,600	0.05623	0.05699	5.91
10^{-5}	0.030	3,600	0.05623	0.05773	5.85
10^{-3}	0.030	3,600	0.05623	0.05690	5.83
10^{-1}	0.030	3,600	0.05623	0.05725	5.89

TABLE X

APPARENT VALENCE OF MOLYBDENUM DISSOLVING ANODICALLY IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 IN THE PRESENCE OF CHLORIDE IONS AT 25°C

Cl^- (N)	c. d. ($amp \cdot cm^{-2}$)	Time (sec)	Weight-loss of Mo Calc (gm)	Weight-loss of Mo Expt (gm)	Apparent Valence
0	0.003	36,000	0.05623	0.05680	5.94
10^{-5}	0.003	28,800	0.04498	0.04584	5.89
10^{-3}	0.003	39,960	0.06242	0.06264	5.98
10^{-1}	0.003	36,000	0.05623	0.05534	6.10
0	0.030	3,600	0.05623	0.05722	5.90
10^{-5}	0.030	3,600	0.05623	0.05623	5.99
10^{-3}	0.030	3,600	0.05623	0.05594	6.03
10^{-1}	0.030	3,600	0.05623	0.05656	5.97

TABLE XI

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 1.0 N KOH AT 25°C (Run 1)

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.650	-0.370	0.000	0.000
0.625	-0.345	0.006	0.003
0.615	-0.335	0.018	0.009
0.59	-0.31	0.055	0.028
0.58	-0.30	0.089	0.045
0.57	-0.29	0.135	0.068
0.56	-0.28	0.222	0.111
0.54	-0.26	0.495	0.248
0.51	-0.23	1.250	0.63
0.48	-0.20	4.00→	2.00→
0.47	-0.19	8.60→	4.30→
0.44	-0.16	26.00	13.00
0.42	-0.14	34.00	17.00
0.40	-0.12	46.00	23.00
0.35	-0.07	48.00	24.00
0.30	-0.12	48.00	24.00

* The area of anode is 2 cm^2

→ Current unsteady after 2 hrs operation

TABLE XII

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 1.0 N KOH AT 25°C (RUN 2)

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.60	-0.32	0.03	0.015
0.57	-0.29	0.10	0.050
0.54	-0.26	0.35	0.177
0.50	-0.22	1.60	0.8
0.47	-0.19	--	--
0.05	-0.17	--	--

* The area of anode is 0.5 cm^2

-- Current unsteady after 2 hrs operation

TABLE XIII

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 1.0 N KOH IN THE PRESENCE OF 10^{-5} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.656	-0.37	0.00	0.00
0.550	-0.27	0.30	0.15
0.530	-0.25	0.65	0.32
0.51	-0.23	1.25	0.62
0.48	-0.20	3.60	1.8
0.46	-0.18	6.0→	3.0→
0.445	-0.16	16.0→	8.0→
0.42	-0.14	36.5	18.2
0.405	-0.12	50.0	25.0
0.37	-0.11	50.4	25.2

* The area of anode is 2 cm^2

→ Current unsteady after 2 hrs operation

TABLE XIV

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 1 N KOH IN THE PRESENCE OF 10^{-3} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.645	-0.365	0.00	0.00
0.570	-0.290	0.11	0.05
0.550	-0.270	0.24	0.12
0.535	-0.255	0.46	0.23
0.520	-0.240	0.80	0.40
0.505	-0.225	1.22	0.61
0.490	-0.210	4.00→	2.00→
0.475	-0.195	9.00→	4.50→
0.460	-0.180	16.00→	8.00→
0.440	-0.160	34.00	17.00
0.435	-0.155	50.40	25.20
0.420	-0.140	80.00	40.00
0.400	-0.120	80.00	40.00

* The area of anode is 2 cm^2

→ Current unsteady after 2 hrs operation

TABLE XV

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 1 N KOH IN THE PRESENCE OF 10^{-1} N Cl^{-} AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.633	-0.353	0.000	0.000
0.610	-0.330	0.020	0.010
0.600	-0.320	0.045	0.022
0.590	-0.310	0.075	0.037
0.580	-0.300	0.118	0.059
0.570	-0.290	0.140	0.070
0.560	-0.280	0.205	0.102
0.550	-0.270	0.332	0.166
0.540	-0.260	0.478	0.239
0.530	-0.250	0.660	0.330
0.520	-0.240	0.910	0.450
0.510	-0.230	1.800→	0.900→
0.490	-0.210	4.000→	2.000→
0.470	-0.190	12.000→	6.000→
0.450	-0.170	22.000→	11.000→
0.435	-0.550	50.000	25.000
0.420	-0.140	75.000	37.000
0.400	-0.120	80.000	40.000

* The area of anode is 2 cm^2

→ Current unsteady after 2 hrs operation

TABLE XVI

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.1 N KOH AT 25°C (RUN 1)

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.542	-0.262	0.000	0.000
0.510	-0.230	0.019	0.038
0.495	-0.215	0.040	0.080
0.48	-0.20	0.074	0.148
0.47	-0.19	0.105	0.21
0.46	-0.18	0.145	0.145

* The area of anode is 0.5 cm^2

TABLE XVII

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.1 N KOH AT 25°C (RUN 2)

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density (mA·cm^{-2})
0.540	-0.260	0.000	0.000
0.515	-0.235	0.015	0.030
0.49	-0.21	0.036	0.072
0.47	-0.19	0.100	0.200
0.45	-0.17	0.015-0.125	0.03-0.25
0.40	-0.12	0.15-0.30	0.30-0.60
0.35	-0.07	0.40→	0.80→
0.32	-0.04	0.70→	1.40→
0.29	-0.01	1.00→	2.00→
0.25	0.03	1.25→	2.50→
0.15	0.13	3.00→	6.00→
0.05	0.23	7.00→	4.00→
-0.05	0.33	9.00	18.00
-0.15	0.43	9.00	18.00
-0.20	0.48	9.00	18.00
-0.30	0.58	9.00	18.00
-0.45	0.73	9.00	18.00

* The area of anode is 0.5 cm^2

→ The current unsteady after 2 hrs operation

TABLE XVIII

GALVANOSTATIC STUDY OF THE DISSOLUTION POTENTIAL OF MOLYBDENUM IN 1.0 N KOH AT 25°C

Current Density ($ma \cdot cm^{-2}$)	t (min)	V (volts, SHE)
0.000	0	−0.380
0.000	15	−0.370
0.000	30	−0.370
0.008	0	−0.220
0.008	15	−0.200
0.008	30	−0.200
0.014	0	−0.182
0.014	15	−0.172
0.014	30	−0.171
0.020	0	−0.168
0.020	15	−0.165
0.020	30	−0.165
0.030	0	−0.163
0.030	15	−0.155
0.030	30	−0.155
0.038	0	−0.152
0.038	15	−0.148
0.038	30	−0.143
0.038	45	−0.140
0.038	60	−0.140
0.042	0	−0.134
0.042	15	−0.131
0.042	30	−0.130
0.048	0	−0.120
0.048	15	−0.113
0.048	30	−0.108
0.048	45	−0.105
0.048	60	−0.105
0.052	0	−0.090
0.052	15	−0.030
0.052	30	--
0.052	31	--
0.056	0	--
0.056	2	--
0.056	4	--
0.060	0	--
0.060	2	--
0.060	4	--

-- Potential cycled from 0.9 volts to 90 volts

TABLE XIX

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.667 N K_2CO_3 AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.542	−0.262	0.00	0.00
0.445	−0.165	0.11	0.05
0.420	−0.140	0.25	0.12
0.400	−0.120	0.44	0.22
0.385	−0.105	0.60	0.30
0.370	−0.090	0.84	0.42
0.350	−0.070	1.25	0.63
0.335	−0.055	1.65	0.83
0.320	−0.04	3.20	1.60
0.300	−0.02	5.00	2.50
0.280	0.000	6.80	3.40
0.265	0.015	9.50	4.75
0.250	0.030	11.5	5.75
0.230	0.050	15.5	7.25
0.210	0.070	19.2	9.60
0.170	0.110	22.0	11.0
0.140	0.140	23.5	11.75
0.100	0.180	22.0	11.0
0.070	0.210	22.1	11.05

* The area of anode is 2 cm^2

TABLE XX

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.667 N K_2CO_3 IN THE PRESENCE OF 10^{-5} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.550	-0.270	0.00	0.00
0.470	-0.190	0.04	0.02
0.430	-0.150	0.19	0.095
0.400	-0.120	0.395	0.198
0.380	-0.100	0.62	0.31
0.350	-0.070	1.2	0.60
0.320	-0.040	2.1	1.05
0.280	0.000	6.4	3.20
0.255	0.025	10.5	5.25
0.230	0.050	15.5	7.75
0.210	0.070	20.0	10.0
0.190	0.090	23.0	11.5
0.170	0.110	25.0	12.5
0.140	0.140	26.0	13.0

* The area of anode is 2 cm^2

TABLE XXI

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.667 N K_2CO_3 IN THE PRESENCE OF 10^{-3} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.56	-0.280	0.000	0.000
0.48	-0.20	0.044	0.022
0.45	-0.17	0.22	0.061
0.435	-0.155	0.190	0.095
0.42	-0.14	0.30	0.15
0.405	-0.125	0.425	0.213
0.39	-0.11	0.605	0.302
0.375	-0.095	0.76	0.38
0.36	-0.08	0.08	0.54
0.34	-0.06	1.75	0.88
0.32	-0.04	2.6	1.3
0.30	-0.02	3.95	1.98
0.28	0.00	6.4	3.2
0.26	0.02	8.6	4.2
0.24	0.04	12.0	6.0
0.22	0.06	14.4	7.2
0.20	0.08	17.0	8.5
0.17	0.11	20.0	10.0

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* The area of anode is a cm^2

TABLE XXII

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.667 N K_2CO_3 IN THE PRESENCE OF 10^{-1} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.55	-0.27	0.000	0.000
0.49	-0.21	0.034	0.017
0.48	-0.20	0.056	0.028
0.45	-0.17	0.11	0.055
0.43	-0.15	0.20	0.10
0.41	-0.13	0.36	0.18
0.39	-0.11	0.64	0.32
1.37	-0.09	0.90	0.45
0.35	-0.07	1.30	0.65
0.33	-0.05	1.82	0.91
0.32	-0.04	3.44	1.72
0.21	0.00	5.1	2.55
0.26	0.02	8.0	4.0
0.24	0.04	10.4	5.2
0.21	0.07	15.0	7.5
0.18	0.10	18.0	9.0
0.15	0.13	20.0	10.0
0.11	0.17	21.0	10.5
0.07	0.21	21.0	10.5
0.03	0.25	21.4	10.7
0.00	0.28	22.0	11.0

* The area of anode is 2 cm^2

TABLE XXIII

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.418	-0.138	0.000	0.000
0.35	-0.07	0.019	0.095
0.32	-0.04	0.026	0.013
0.29	-0.01	0.028	0.014
0.26	0.02	0.028	0.014
0.21	0.07	0.032	0.016
0.18	0.10	0.034	0.017
0.14	0.14	0.046	0.023
0.11	0.17	0.066	0.033
0.08	0.20	0.096	0.048
0.05	0.23	0.134	0.067
0.02	0.26	0.182	0.091
-0.01	0.29	0.26	0.13
-0.04	0.32	0.38	0.19
-0.07	0.35	0.62	0.31
-0.10	0.38	1.06	0.53
-0.13	0.41	1.8	0.9
-0.16	0.44	3.2	1.6
-0.19	0.47	5.0	2.5
-0.22	0.50	6.0	3.0
-0.25	0.53	6.0	3.0
-0.28	0.56	7.4	3.7
-0.32	0.60	11.0	5.5

* The area of anode is 2 cm^2

TABLE XXIV

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 IN THE PRESENCE OF 10^{-5} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.41	-0.13	0.000	0.000
0.19	0.09	0.013	0.065
0.16	0.12	0.022	0.011
0.13	0.15	0.038	0.019
0.10	0.18	0.060	0.030
0.07	0.21	0.082	0.041
0.04	0.24	0.10	0.05
0.00	0.28	0.16	0.08
-0.02	0.30	0.20	0.10
-0.04	0.32	0.28	0.14
-0.06	0.34	0.38	0.19
-0.08	0.36	0.56	0.28
-0.10	0.38	0.78	0.39
-0.12	0.40	1.04	0.52
-0.14	0.42	1.46	0.73
-0.16	0.44	2.0	1.0
-0.18	0.46	2.2	1.1
-0.20	0.48	2.4	1.2
-0.24	0.52	2.6	1.3
-0.26	0.54	2.6	1.3
-0.28	0.56	3.0	1.5
-0.31	0.59	4.2	2.1

* The area of anode is 2 cm^2

TABLE XXV

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 IN THE PRESENCE OF 10^{-3} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.40	-0.12	0.000	0.000
0.31	-0.03	0.018	0.009
0.27	0.01	0.022	0.011
0.23	0.05	0.022	0.011
0.20	0.08	0.026	0.013
0.18	0.10	0.028	0.014
0.14	0.14	0.038	0.019
0.11	0.17	0.060	0.030
0.08	0.20	0.086	0.042
0.05	0.23	0.125	0.063
0.03	0.25	0.150	0.075
0.01	0.27	0.185	0.093
-0.01	0.29	0.24	0.12
-0.03	0.31	0.36	0.16
-0.05	0.33	0.48	0.23
-0.07	0.35	0.60	0.30
-0.09	0.37	0.88	0.44
-0.11	0.39	1.20	0.60
-0.13	0.41	1.64	0.82
-0.15	0.43	2.4	1.2
-0.17	0.45	3.4	1.7
-0.19	0.47	4.6	0.3
-0.21	0.49	3.8	1.9
-0.25	0.53	--	--
-0.27	0.55	0.85	0.43
-0.29	0.57	1.2	0.60
-0.33	0.61	2.7	1.35
-0.35	0.63	4.2	2.10

* The area of anode is 2 cm^2

--Current unsteady (decreasing) after 3 hrs operation

TABLE XXVI

CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF MOLYBDENUM IN 0.001 N K_2CO_3 + 0.666 N K_2SO_4 IN THE PRESENCE OF 10^{-1} N Cl^- AT 25°C

V_m (volts, NCE)	V (volts, SHE)	Current* (mA)	Current Density ($mA \cdot cm^{-2}$)
0.414	−0.134	0.000	0.000
0.34	−0.00	0.025	0.013
0.30	−0.02	0.038	0.019
0.23	0.05	0.040	0.020
0.19	0.09	0.045	0.023
0.16	0.12	0.050	0.025
0.13	0.15	0.060	0.030
0.10	0.18	0.084	0.042
0.08	0.20	0.105	0.053
0.05	0.23	0.155	0.078
0.02	0.26	0.22	0.11
−0.01	0.29	0.28	0.14
−0.04	0.32	0.46	0.23
−0.07	0.35	0.66	0.33
−0.09	0.37	0.95	0.48
−0.12	0.40	1.55	0.78
−0.14	0.42	2.2	1.1
−0.16	0.44	2.8	1.4
−0.19	0.47	4.6	2.3
−0.22	0.50	5.0	2.5
−0.25	0.53	5.4	2.7

VII. BIBLIOGRAPHY

1. Marino, L., Gazetta Chimica Italiana, 35 II, 193 (1905).
2. Kuessner, V.H. Zeitschrift Fur Elektrochemie, 18, 754 (1910).
3. Thompson, M. and A.L. Kaye, Trans. Am. Electrochem. Soc., 61, 255 (1932).
4. Morral, F.R. and J.L. Bray, Trans. Am. Electrochem. Soc., 75, 427 (1939).
5. Blavatnik, V.M., M.M. Dolganova and V.N. Begishev, Usb. Khum. Zh., 11(1), 54 (1967):
   Chem. Abs., 66, 121496n (1967).
6. Gladysheva, V.P. and A.Y. Shatalov, Izv. Vysshikh Uchebn. Zavednii, Khim. i Khim. Teknol. 9(1), 48 (1966):
   Chem. Abs., 65, 5002a (1966).
7. Besson, J. and G. Drautzburg, Electrochemica Acta. 3, 158 (1960).
8. Masing, G. and G. Röth, Werkstoffe U. Korrosion 3, 176 (1952).
9. Shatalov, A.Y., Doklady Akad. Nauk. S.S.S.R., 86, 775 (1953):
   Chem. Abs., 47, 3752b (1953).
10. Shatalov, A.Y. and I.A. Marshakov, Zhur. Fiz. Khim., 28, 42 (1954):
    Chem. Abs., 48, 8084f (1954).

11. Pozdeeva, A.A., E.I. Antonovskaya, and A.M. Sukhotin, Corrosion Science 6, 149 (1966).

12. Eidman, E.I., Tr. Molodych Uch., Saratov. Univ. Vyp. Saratav 66 (1965):
Chem. Abs., 66, 43062b (1965).

13. Cotton, F.A. and G. Wilkinson, Advanced Inorganic Chem., p. 780, Interscience Publisher, London (1962).

14. Deltombe, E., N. DeZoubov and M. Pourbzix, p. 275, Atlas of Electrochemical Equilibrium in Aqueous Solution. Pergamon Press, London (1966).

15. Chen, C.K., "Anodic Dissolution of Molybdenum in Acid Sulfate Solutions," unpublished thesis, University of Missouri-Rolla.

16. Potter, E.C., Electrochemistry Principles and Application, p. 147, Cleaver-Hume Press Ltd., London (1961).

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