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THE ANODIC DISSOLUTION OF TUNGSTEN

BY

CHING-LUN WU, 1936 -

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A

THESIS

submitted to the Faculty of

UNIVERSITY OF MISSOURI - ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1970

T2509  
46 pages  
c.1

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Approved by

John W. Johnson (Advisor)

W. J. James

T. J. O'Keefe

**180967**

## PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by the Journal of Less-Common Metals. Pages 1-18 will be presented for publication in that journal. Appendices A, B, C, D and E have been added for purposes normal to thesis writing.

## ACKNOWLEDGEMENTS

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

Thanks are extended to the Materials Research Center for the use of equipment.

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

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## THE ANODIC DISSOLUTION OF TUNGSTEN

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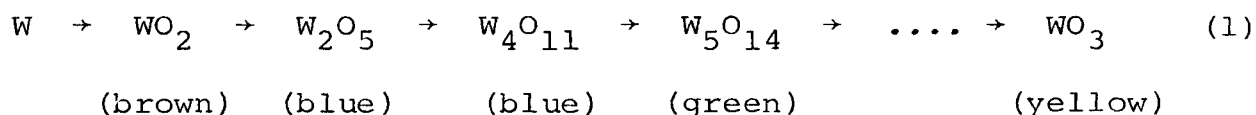
Abstract

The anodic dissolution of tungsten was studied in  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  solutions (pH = -2 to 2.5) and  $\text{K}_2\text{SO}_4$ - $\text{K}_2\text{CO}_3$ -KOH solutions (pH = 11.5 to 14.5) at 25°C. Faradaic efficiency studies in basic solutions showed that the metal was oxidized to the +6 state. In acid solutions, a thick protective film of yellow  $\text{WO}_3$  was formed. Polarization measurements showed linear Tafel behavior (slope  $\approx 2.3RT/F$ ) in the potential region slightly more positive than the rest potentials. An anodic dissolution mechanism is proposed which involves a surface film of  $\text{W}_2\text{O}_5$  that is further oxidized to  $\text{WO}_3$  and dissolves by hydrolyzation.

Introduction

Studies of the electrochemical behavior of W have appeared infrequently in the literature for over 100 years.

A bibliography and brief review of much of the early work appears in a paper by Koerner.<sup>1</sup> Koerner also reported extensive open-circuit potential measurements of the W electrode and observations of its anodic behavior in various acids and bases. The potentials were dependent on the type of metal used, the electrolyte pH, and also showed some variation with the nature of the electrolyte. The former dependence was attributed to the presence of appreciable oxides in the metal and the latter to the effect of specific ions on the solubility of the dissolved W species, primarily  $W(OH)_6$ . This compound was believed to break down to tungstic cations in acidic electrolytes and anions in basic. Upon commencing polarization in acid electrolytes, films were formed on the W surface whose color changed through a definite sequence. These colors were associated with tungsten oxides of progressively higher oxygen content, i.e.,

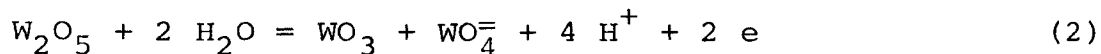


The passiveness of W in acids was attributed to low solubilities of the oxides in this media and the activeness in bases to high solubilities. A valence of +6 was determined for W dissolving in  $NH_4OH-NH_4Cl$  solutions.

Thompson and Rice<sup>2</sup> studied the anodic and cathodic behavior of W in KOH solutions. During anodic dissolution,

near 100% current efficiencies were found for the oxidation to the W-VI state, even though extremely high polarization (20-100 V) occurred in many cases. The break in the polarization curves where the overvoltage rapidly increased was dependent on both c.d. and  $C_{OH^-}$ .

El Wakkad, et. al.,<sup>3</sup> studied the behavior of W in various buffer solutions. They found the potentials of massive W and powdered W-WO<sub>3</sub> electrodes to correspond closely. A discontinuity in the E-pH relation was noted at pH's 4-6. It was proposed that the potentials in neutral and basic solutions were controlled by the reaction.



The discontinuity was attributed to an incompleteness of the reduction portion of the reaction (eq. 2) in acid solution with tungsten blue (W<sub>3</sub>O<sub>8</sub> or W<sub>4</sub>O<sub>11</sub>) being the product rather than W<sub>2</sub>O<sub>5</sub>. The effect of pH on potential ( $\partial E/\partial pH$ ) as shown in various plots was ca. 50 mv. It was proposed that W dissolves as  $WO_4^-$  in strong bases and  $WO_2^{++}$  in strong acids.

Besson and Drautzburg<sup>4</sup> have also reported a study of the anodic dissolution of W in various electrolytes. The oxidation of W was found to proceed quantitatively to the +6 state. Agitation of the electrolyte displaced the Tafel curves. Tafel slopes were reported for both acidic

and basic electrolytes that ranged from 55 to 150 mv.

The present study was undertaken in an attempt to establish a more detailed anodic dissolution mechanism for W. It was also of interest to see if a mechanism recently proposed for Mo<sup>5</sup>, a chemically similar metal, would be applicable.

### Experimental

The tungsten anodes were prepared from cylindrical specimens cut from a rod of 0.75 inch diameter.\* They were polished on grinding paper down to 600 grit, cleaned in distilled water with ultrasonic agitation, rinsed with distilled water and acetone, dried, and then mounted in a teflon holder. All solutions employed analytical grade chemicals and distilled water. The electrolyses were carried out in an H-cell containing approximately 300 ml of electrolyte at  $25.0 \pm 0.1^\circ\text{C}$ . Prepurified nitrogen was bubbled through the electrolyte to purge air from the system and for stirring. The reference electrodes were Hg/Hg<sub>2</sub>SO<sub>4</sub> (1 N H<sub>2</sub>SO<sub>4</sub>) for acidic and Hg/Hg<sub>2</sub>Cl<sub>2</sub> (1 N KCl) for basic electrolytes. A salt bridge of the same electrolyte as in the electrolysis cell was used to prevent contamination by the reference electrode. All potentials are

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\*Electronic Space Products, Inc., 4N grade (99.99% purity).  
Typical analysis (ppm): Ca 10, Cu <10, Mg <10, Mo <50,  
Si <50, Cb <10, Fe <20, Mn 10, Ni <30, Ti <10.

reported versus the standard hydrogen electrode (SHE) at 25°C.

### Results

Self-dissolution experiments were carried out initially with the W anodes kept in the cell at open-circuit for 24 hours. No detectable weight losses were noted except for 1 and 3 N KOH. In these latter electrolytes, an anode with an exposed area of 2.84 cm<sup>2</sup> lost approximately 5 mg during the 24 hour period.

Polarization Measurements. The anodic polarization behavior for W was determined potentiostatically in acidic and basic electrolytes and is illustrated in Fig. 1. The curves contain linear (Tafel) sections in the potential region just above the rest potentials. Both the Tafel slopes and the rest potentials are tabulated in Table I. In the acid electrolytes, the active dissolution regions were quite small and limiting currents of  $10^{-5}$  -  $10^{-4}$  amp·cm<sup>-2</sup> were reached at relatively low overpotentials. Visible oxygen evolution commenced from the anode at potentials of 1.3-2.0 volts. A lemon-yellow film was formed on the electrode during polarization and was identified by X-ray analysis as WO<sub>3</sub>. A high-voltage power supply in a galvanostatic arrangement was used to polarize the W anode in 3 N H<sub>2</sub>SO<sub>4</sub> at c.d.'s greater than the limiting values mentioned above. The results are shown in Fig. 2.

The yellow surface film thickened visibly and oxygen was evolved vigorously. At the higher c.d.'s, the potential continually fluctuated by 5-10 volts.

In basic electrolytes, the active dissolution region covered a much larger range of c.d.'s. No films nor limiting currents were observed.

Valence Measurements. The results of the valence determinations in both acidic and basic media are shown in Table II. In the acidic media, oxygen could be seen evolving at all but the lowest current densities. The smallness of the limiting currents precluded an accurate determination of the oxidation state of the dissolving W ions in the active dissolution region. The weight loss for a c.d. of  $10^{-4}$  amp·cm<sup>-2</sup> (which occurred over a period of several days) corresponded to a W valence (oxidation state) of 22. Apparently oxygen was also being produced at this c.d., but at such a low rate that it dissolved without bubble formation. It should be noted, though, that significant weight losses of the metal occurred even during visible oxygen evolution at high c.d.'s. This indicates the absence of any effective anodic passivation region.

The oxidation state of W species entering into solution in basic electrolytes is very close to +6 within experimental error. It appears to be independent of both pH and c.d., and is in agreement with values reported by other investigators.

### Discussion

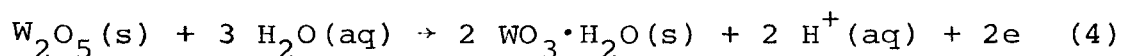
In alkaline media, the apparent valence data indicate that tungsten goes into solution according to the overall reaction:



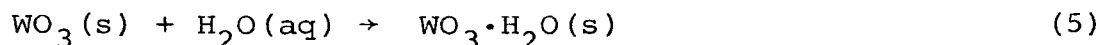
Qualitative tests of the anolytes showed the presence of  $WO_4^-$ , as expected from the absence of color and in accord with thermodynamic data indicating it to be a stable ion at these conditions.<sup>6-8</sup> In acid media, the yellow film formed on the electrode surface and identified as  $WO_3$  also indicated that oxidation resulted in the +6 state. The formation of this oxide, which is both relatively insoluble and non-conductive, explains the small potential-independent currents that were observed. The fact that W dissolved over the entire potential region (Tafel, limiting current, and oxygen evolution) is evidence of a slight solubility of the oxide as no pitting developed indicating a porous film. The dissolution is probably accomplished through a hydration reaction to form  $WO_3 \cdot H_2O$  (or tungstic acid  $H_2WO_4$ ).

The open-circuit "rest" potentials of the W electrode (shown in Fig. 3) are a function of pH. The value  $\partial V_{rest} / \partial pH \approx 0.059 \text{ V} = 2.3 \text{ RT/F}$ , indicates a 1:1 ratio of  $H^+$  to electrons in the electrochemical step that is controlling the rest potential. As also seen in Fig. 3, the measured values do not correspond to any of the relations for various

W-H<sub>2</sub>O equilibria that are available from the literature.<sup>9,10</sup> They agree reasonably well with the values reported by El Wakkad, et. al.,<sup>3</sup> but not with the pH effect from his proposed reaction (eq. 2). The slight solubility of WO<sub>3</sub> as well as previous findings regarding Mo<sup>5</sup>, a chemically similar metal, suggest an equilibrium between W<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>·H<sub>2</sub>O as a possibility, i.e.,



Data are not available pertaining to the standard free energy of formation of WO<sub>3</sub>·H<sub>2</sub>O, but an approximate value can be obtained by estimating the free energy change, i.e.,  $\Delta G_{hyd}^{\circ}$ , for the following reaction:



An examination of the data for a large number of mono-hydrated compounds of compositions MO<sub>x</sub>·H<sub>2</sub>O, H<sub>2</sub>MO<sub>y</sub>, and M(OH)<sub>2</sub> shows that the free energy changes for the reactions of the oxides with water are usually within the limits of  $\pm 10$  Kcal. For compounds normally found in the hydrated form (e.g., CrO<sub>3</sub>, MgO, MnO),  $-10 < \Delta G_{hyd}^{\circ} < 0$  Kcal, while for compounds normally found in the anhydrous form (e.g., TeO<sub>2</sub>, GeO<sub>2</sub>, SiO<sub>2</sub>),  $0 < \Delta G_{hyd}^{\circ} < 10$  Kcal. Since anhydrous WO<sub>3</sub> is reported to be the normally stable form, its free energy of hydration will be positive and can be estimated to be



5-10 Kcal. For the following calculations,  $7.5 \pm 2.5$  Kcal will be used. Thus,

$$\begin{aligned}\Delta G_{f, \text{WO}_3 \cdot \text{H}_2\text{O}}^{\circ} &= \Delta G_{f, \text{WO}_3}^{\circ} + \Delta G_{f, \text{H}_2\text{O}}^{\circ} + \Delta G_{\text{hyd}}^{\circ} & (6) \\ &= -182,740 + (-56,690) + (7,500 \pm 2,500) \\ &= -231,930 \pm 2,500 \text{ cal}\end{aligned}$$

The corresponding  $\Delta G^{\circ}$  for eq. 4 is

$$\begin{aligned}\Delta G^{\circ} &= \Delta G_{f, \text{W}_2\text{O}_5}^{\circ} + 3 \Delta G_{f, \text{H}_2\text{O}}^{\circ} - 2 \Delta G_{f, \text{WO}_3 \cdot \text{H}_2\text{O}}^{\circ} & (7) \\ &= (-306,900) + 3(-56,690) - 2(-231,930 \pm 2,500) \\ &= -13,110 \pm 5,000\end{aligned}$$

The Nernst relationship for this reaction is

$$\begin{aligned}E &= (+0.3 \pm 0.1) - \frac{2.3RT}{F} \log \frac{1}{a_{\text{H}^+}} & (8) \\ &= (+0.3 \pm 0.1) - 0.059 \text{ pH}\end{aligned}$$

The band representing eq. 8 on Fig. 3 includes all the experimental points. A best-fit line through the points yields a free energy change for eq. 5 of +8 Kcal.

With the above information, the anodic dissolution of W can be described qualitatively as follows:

1. When placed in solution, the W electrode very

rapidly forms a film of approximate composition  $W_2O_5$  that completely covers the metal surface. Further spontaneous reaction (corrosion or self-dissolution) ceases except at relatively high pH's where  $W_2O_5$  is soluble.

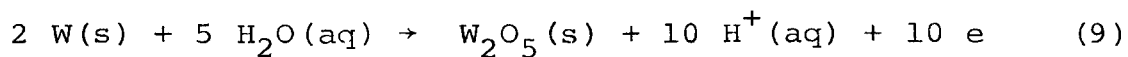
2. Upon polarization, the appreciable conductivity of  $W_2O_5$  allows further electrochemical oxidation to  $WO_3$ .

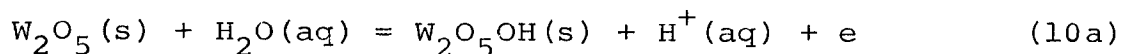
3. The solvation of  $WO_3$  is accomplished by hydration to  $WO_3 \cdot H_2O$  (or  $H_2WO_4$ ) which has a very low conductivity, is only slightly soluble in acids, and is appreciably soluble in bases.

4. The limiting (potential independent) curves in acidic electrolytes can be attributed to an insulating layer of  $WO_3$  which accumulates due to its low insolubility. The absence of a limiting current in basic electrolytes is due to the solubility of  $WO_3$  in this media.

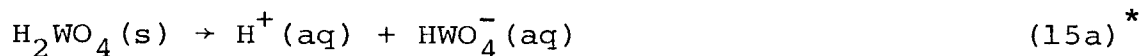
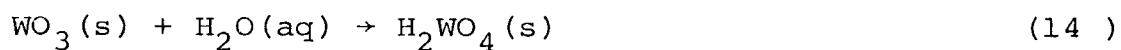
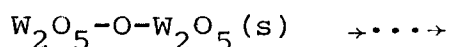
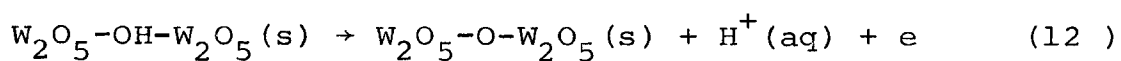
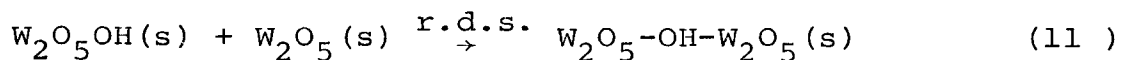
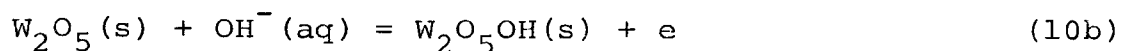
5. The rapid complete coverage of the metal surface by  $W_2O_5$  indicates the experimental kinetic parameters are associated with its further oxidation. The Tafel slope of  $\sim 60$  mv is thus associated with a chemical rate-determining step subsequent to the first electron transfer from  $W_2O_5$ . The pH effect indicates the production of hydrogen ions (or their equivalent) prior to the r.d.s.

Expressing the above in equation form gives:

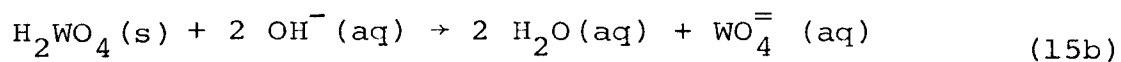




and/or



and/or



The oxygen-bridged W compounds ( $W_2O_5$ ,  $W_4O_{11}$ , etc.) are known to exist and were incorporated in the sequence postulated previously for the anodic dissolution of Mo.

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\*Or possibly  $H_2WO_4 + 2 H^+ \rightarrow WO_2^{++} + 2 H_2O$

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TABLE I

REST POTENTIALS AND TAFEL SLOPES FOR THE ANODIC  
DISSOLUTION OF TUNGSTEN AT 25°C

Electrolyte	pH	Rest Potential	Tafel Slope
gmequiv/liter		Volts (SHE)	Volts
10.0 H <sub>2</sub> SO <sub>4</sub>	-2	0.29	0.060
3.0 H <sub>2</sub> SO <sub>4</sub>	-0.5	0.28	0.060
1.0 H <sub>2</sub> SO <sub>4</sub>	0.38	0.27	0.058
0.24 H <sub>2</sub> SO <sub>4</sub> + 0.76 K <sub>2</sub> SO <sub>4</sub>	1.5	0.235	0.065
0.1 H <sub>2</sub> SO <sub>4</sub> + 0.9 H <sub>2</sub> SO <sub>4</sub>	2.5	0.22	0.058
1.0 K <sub>2</sub> CO <sub>3</sub>	11.5	-0.38	0.072
0.1 KOH + 0.9 K <sub>2</sub> SO <sub>4</sub>	12.7	-0.41	0.060
1.0 KOH	13.6	-0.42	0.060
3.0 KOH	14.5	-0.47	0.058

TABLE I I  
 COULOMBIC DATA FOR THE ANODIC DISSOLUTION  
 OF TUNGSTEN AT 25°C

Electrolyte	Time	Current Density	Weight-loss		Apparent Valence	Effi- ciency	
			Expt.	Cal.			
gmequiv/liter	sec	amp·cm <sup>-2</sup>	gm	gm		percent	
1 N H <sub>2</sub> SO <sub>4</sub>	554400	0.0001	0.01334	0.05		26.6**	
	554400	0.001	0.01278	0.05		25.4	
	18480	0.003	0.01014	0.05		20.3	
	18480	0.003	0.01060	0.05		21.2	
	5543	0.010	0.00974	0.05		19.5	
	11086	0.010	0.01870	0.10		18.7	
	1664	0.050	0.01143	0.075		15.2	
	1109	0.050	0.00688	0.05		13.8	
	0.1 N KOH + 0.9 N K <sub>2</sub> SO <sub>4</sub>	27720	0.002	0.04995	0.05	6.00	
		27720	0.002	0.05025	0.05	5.97	
1 N KOH	27720	0.002	0.05134	0.05	5.86		
	55440	0.002	0.10224	0.10	5.85		
	5543	0.010	0.04963	0.05	6.04		
	5543	0.010	0.04929	0.05	6.07		
	1109	0.050	0.05033	0.05	5.97		
	2218	0.050	0.10182	0.10	5.89		
	5543	0.010	0.05042	0.05	5.95		
11086	0.010	0.10160	0.10	5.91			

\*Area of the electrode = 2.84 cm<sup>2</sup>

\*\*Coulombic efficiency based on W-VI oxidation state

## CAPTIONS FOR FIGURES

1. Anodic polarization of tungsten in aqueous solutions at 25°C.  
(o, pH = -2.0;  $\Delta$ , pH = -0.5;  $\nabla$ , pH = 0.38 (run 1);  
 $\nabla$ , pH = 0.38 (run 2);  $\square$ , pH = 1.5;  $\diamond$ , pH = 2.5;  
 $\bullet$ , pH = 11.5;  $\blacktriangle$ , pH = 12.7;  $\blacktriangledown$ , pH = 13.6;  $\blacksquare$ , pH = 14.5).
2. Anodic polarization (galvanostatic) of tungsten in 3 N H<sub>2</sub>SO<sub>4</sub> at 25°C.
3. Comparison of the measured "open-circuit" potentials of the tungsten electrode with the thermodynamic values for various tungsten-water reaction at 25°C.

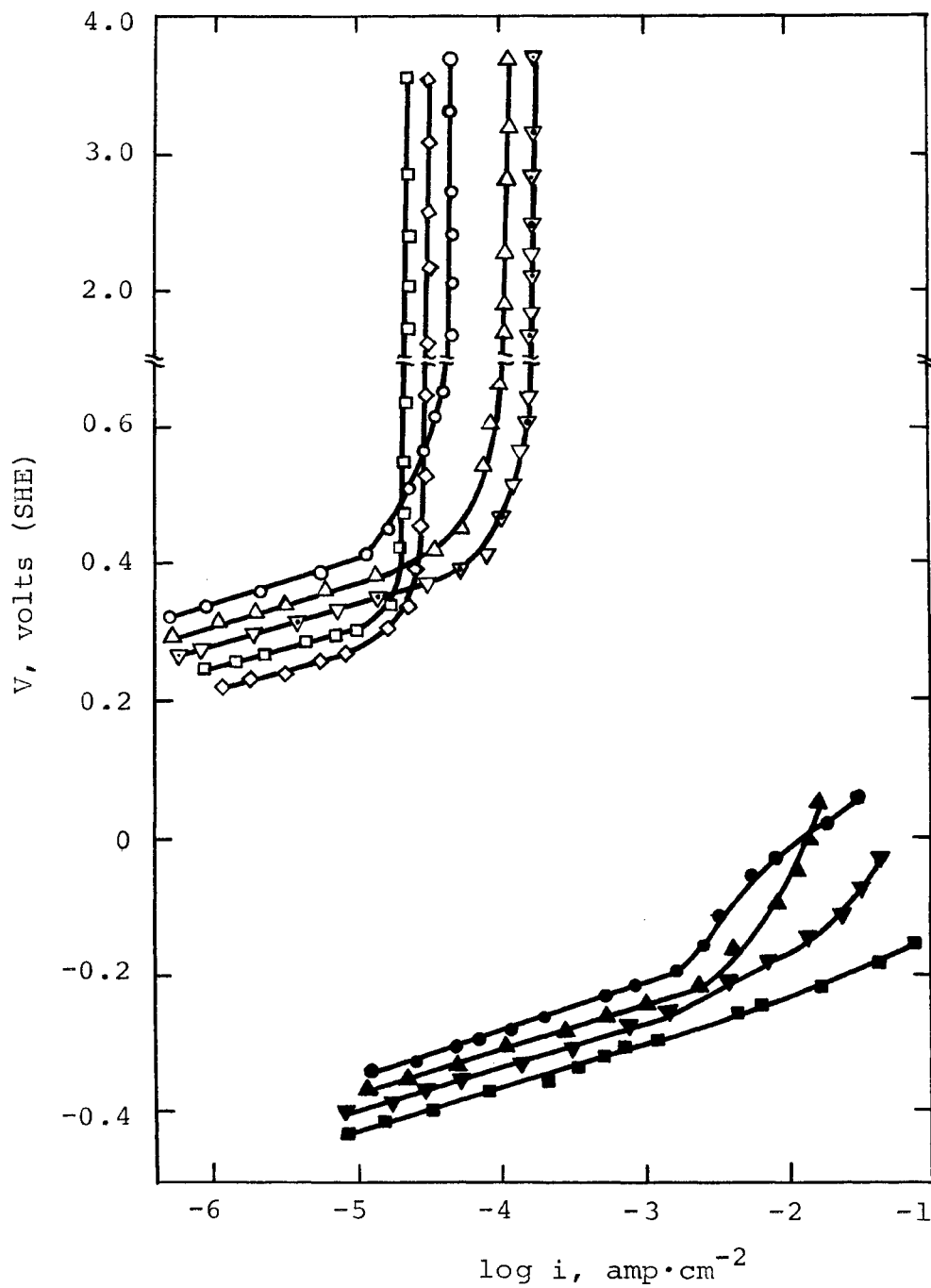


Figure 1. Anodic polarization of tungsten in aqueous solutions at 25°C.



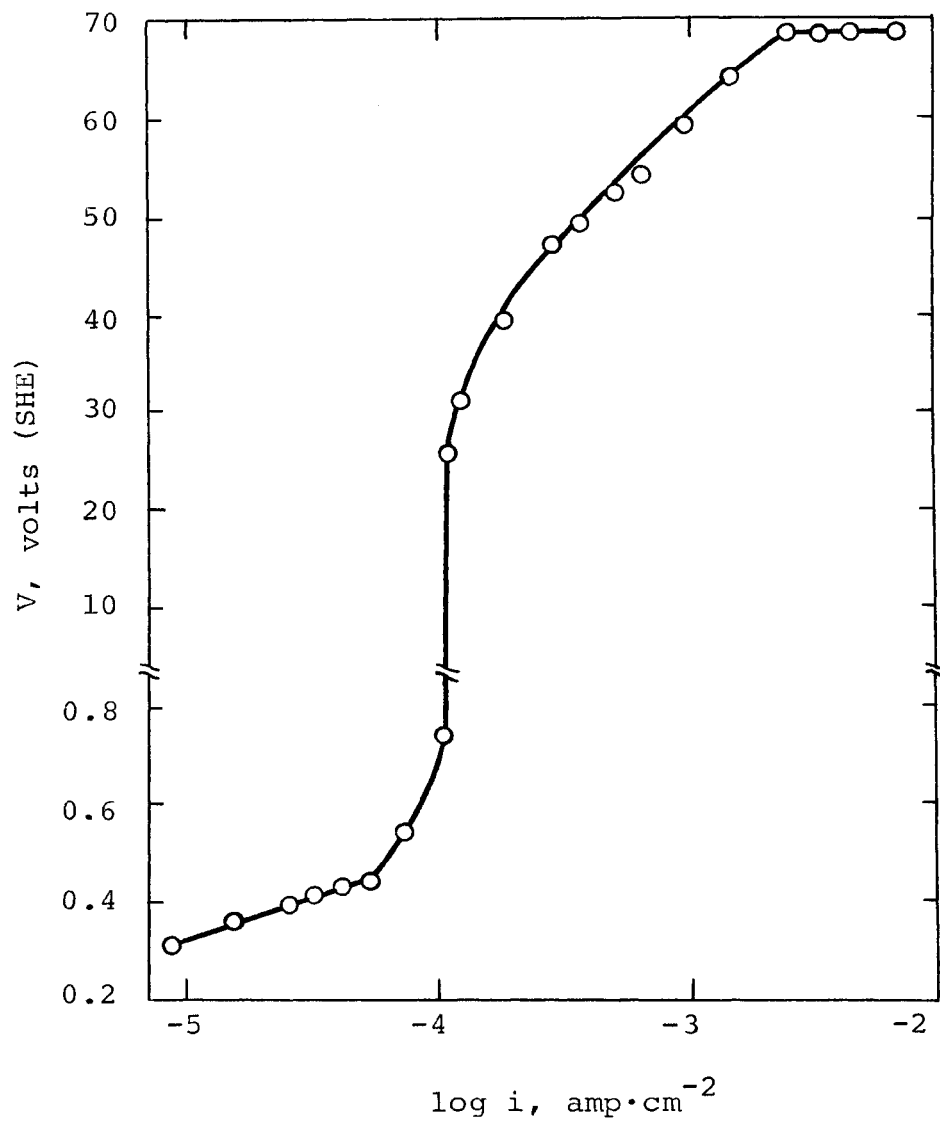


Figure 2. Anodic polarization (galvanostatic) of tungsten in 3 N H<sub>2</sub>SO<sub>4</sub> at 25°C.

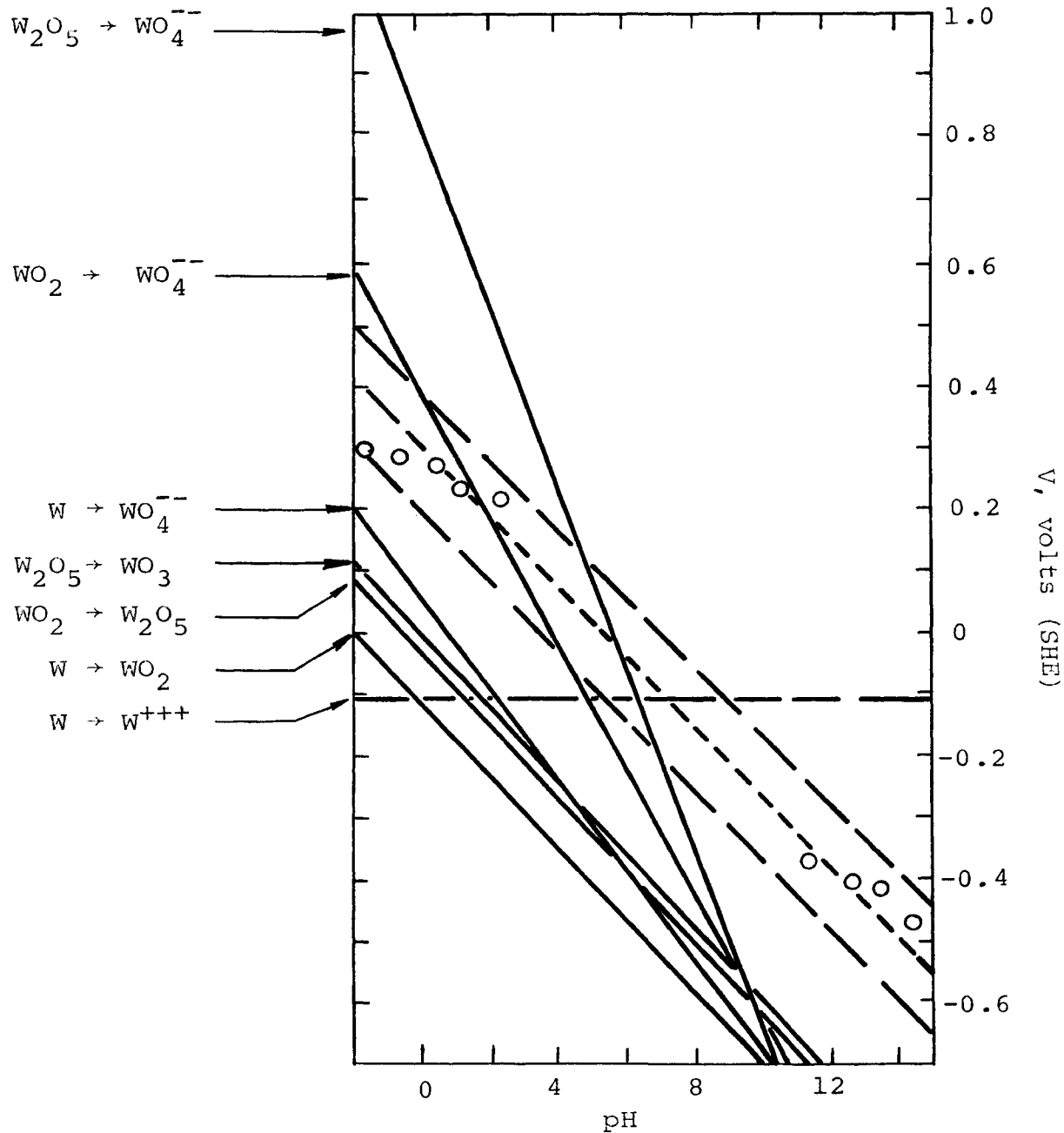


Figure 3. Comparison of the measured "open-circuit" potentials of the tungsten electrode with the thermodynamic values for various tungsten-water reactions at 25°C.

## APPENDIX A

## Materials

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

1. Sulfuric Acid. Reagent grade, meets ACE specifications. Mallinckrodt Co., New York.
2. Potassium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, New Jersey.
3. Potassium Hydroxide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, New Jersey.
4. Potassium Carbonate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fairlawn, New Jersey.
5. Nitrogen. Prepurified grade, Matheson Co., Joliet, Illinois.
6. Tungsten. 0.75 inch rod, 99.99% purity. Electronic Space Products, Inc., Los Angeles, Calif.

## APPENDIX B

## Equipment

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

1. Surface preparation of tungsten specimens.
  - a. Belt Surfacers. Buehler No. 1250. Buehler, Ltd., Evanston, Illinois.
  - b. Hand Grinder. Handimet, 4-stage with grits No. 240, 320, 400, and 600. Buehler No. 1470, Buehler, Ltd., Evanston, Illinois.
  - c. Ultrasonic Cleaner. Model LP-1. Electromotion Component Corp., L.I., New York.
2. Electrolysis Apparatus.
  - a. Power Supply. Model 500r Serial A-1493 Input 105-125 volts 50-60 cycles D.C. regulated volts (0-600 volts), Kepco Laboratories, Inc., Flushing, New York.
  - b. Electrometer. Model 610b, Keithy Instruments Inc., Cleveland, Ohio.
  - c. Ammeter. Model 931, Weston Electric Instruments 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.

- f. pH Meter. Model 19, Fisher Scientific Co.,  
Pittsburgh, Pa.

## APPENDIX C

## X-Ray Diffraction Data

TABLE III

X-RAY DIFFRACTION DATA\* FROM THE TUNGSTEN ELECTRODE  
 SURFACE AFTER ANODIC DISSOLUTION IN 1 N H<sub>2</sub>SO<sub>4</sub> AT  
 $10^{-4}$  amp·cm<sup>-2</sup> AND 25°C

2θ	Exp. "d" Spacings	A.S.T.M. Values for WO <sub>3</sub> **		
degrees	Å°	Å°		I/I <sub>1</sub>
24.6	3.61	3.64		100
28.2	3.16	3.10		50
35.1	2.55	2.52		35
41.0	2.19	2.17		50
59.0	1.56	1.55		30
73.8	1.28	1.28		15
87.7	1.11	1.19		5

\* Radiation: Cu,  $\lambda = 1.542 \text{ \AA}$

\*\* ASTM Card No. 5-0363

TABLE IV

X-RAY DIFFRACTION DATA\* FROM THE TUNGSTEN ELECTRODE  
 SURFACE AFTER ANODIC DISSOLUTION IN 3 N KOH AT  
 $10^{-4}$  amp·cm<sup>-2</sup> AND 25°C

2θ	Exp. "d" Spacings	A.S.T.M.	Values for W**
degrees	Å°	Å°	I/I <sub>1</sub>
41.0	2.15	2.06	80
59.0	1.56	1.45	40
73.8	1.28	1.26	60
87.6	1.11	1.10	70

\* Radiation: Cu,  $\lambda = 1.542$  Å°

\*\* ASTM Card No. 2-1138



APPENDIX D

Anodic Polarization Data

TABLE V

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 10 N H<sub>2</sub>SO<sub>4</sub> (pH = - 2 ) at 25°C

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp · cm <sup>-2</sup>
0.38	0.29	0.0000	0.0000
0.37	0.30	0.0010	0.00056
0.36	0.31	0.0016	0.0009
0.35	0.32	0.0023	0.0013
0.33	0.34	0.0040	0.0025
0.315	0.355	0.0060	0.0035
0.30	0.37	0.0100	0.00565
0.285	0.385	0.0150	0.0085
0.27	0.40	0.0200	0.0114
0.25	0.42	0.0250	0.0130
0.24	0.43	0.0290	0.0165
0.22	0.45	0.0330	0.0187
0.20	0.47	0.0360	0.0204
0.17	0.50	0.0400	0.0227
0.11	0.56	0.0470	0.0266
0.05	0.62	0.0530	0.0304
0.00	0.67	0.0570	0.0320
-0.10	0.77	0.0720	0.0410
-0.20	0.87	0.0720	0.0410
-0.35	1.02	0.0720	0.0410
-0.85	1.52	0.0720	0.0410
-1.00	1.72	0.0720	0.0410
-1.50	2.32	0.0720	0.0410
-2.00	2.67	0.0720	0.0410
-3.00	3.67	0.0720	0.0410

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE VI

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 3 N H<sub>2</sub>SO<sub>4</sub> (pH = -0.5) AT 25°

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.39	0.28	0.0000	0.0000
0.38	0.29	0.0010	0.00056
0.37	0.30	0.0020	0.00113
0.36	0.31	0.0025	0.0014
0.35	0.32	0.0035	0.0019
0.34	0.33	0.0045	0.00256
0.33	0.34	0.0055	0.0031
0.32	0.35	0.0080	0.0045
0.31	0.36	0.0113	0.0058
0.30	0.37	0.0165	0.0090
0.39	0.38	0.0225	0.0130
0.28	0.39	0.0395	0.0220
0.27	0.40	0.0525	0.0300
0.26	0.41	0.0605	0.0340
0.25	0.42	0.0660	0.0370
0.24	0.43	0.0720	0.0410
0.225	0.445	0.0950	0.0540
0.21	0.46	0.100	0.0560
0.18	0.49	0.110	0.0570
0.13	0.54	0.130	0.0740
0.07	0.60	0.150	0.0840
0.00	0.67	0.160	0.0900
-0.09	0.76	0.175	0.0990
-0.18	0.85	0.185	0.104
-0.25	0.92	0.190	0.108
-0.33	1.00	0.190	0.108
-0.75	1.42	0.210	0.120
-1.10	1.77	0.210	0.120
-1.60	2.27	0.215	0.125
-2.00	2.67	0.215	0.125
-3.00	3.67	0.215	0.125

Area of electrode = 1.76 cm<sup>2</sup>

TABLE VII

CURRENT-POTENTIAL DATA (GALVANOSTATIC) FOR THE ANODIC DISSOLUTION OF TUNGSTEN IN 3 N H<sub>2</sub>SO<sub>4</sub> (pH = -0.5) AT 25°C

Current ma	Current Density x 10 <sup>3</sup> amp·cm <sup>-2</sup>	Potential	
		volts (NSE)	volts (SHE)
0.000	0.000	0.39	0.28
0.016	0.0093	0.36	0.31
0.030	0.0170	0.31	0.36
0.050	0.028	0.28	0.39
0.060	0.034	0.27	0.40
0.080	0.045	0.26	0.41
0.115	0.060	0.24	0.43
0.140	0.080	0.125	0.54
0.190	0.102	-0.070	0.74
0.200	0.113	-25.0	25.7
0.240	0.145	-28.0	30.2
0.350	0.200	-38.0	38.7
0.530	0.300	-46.0	46.7
0.700	0.400	-48.0	48.7
0.800	0.450	-50.0	50.7
0.900	0.530	-50.5	51.2
1.23	0.710	-51.5	52.2
1.58	0.900	-53.0	53.7
1.76	1.00	-59.0	59.7
2.64	1.50	-64.0	64.7
4.40	2.50	-68.0	68.7
6.00	3.50	-68.0	68.7
8.00	4.50	-68.0	68.7
12.0	6.80	-68.0	68.7

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE VIII

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 1 N H<sub>2</sub>SO<sub>4</sub> (pH = 0.38) AT 25°C (RUN 1)

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp · cm <sup>-2</sup>
0.38	0.28	0.000	0.000
0.37	0.29	0.001	0.00056
0.36	0.30	0.0035	0.002
0.35	0.31	0.007	0.004
0.34	0.32	0.010	0.0056
0.33	0.33	0.145	0.0082
0.32	0.34	0.020	0.0113
0.31	0.35	0.0275	0.0155
0.30	0.36	0.037	0.0209
0.29	0.37	0.0495	0.0297
0.28	0.38	0.0675	0.0383
0.27	0.39	0.082	0.0465
0.25	0.41	0.125	0.071
0.23	0.43	0.140	0.0835
0.21	0.45	0.170	0.0965
0.18	0.48	0.140	0.0835
0.15	0.51	0.160	0.090
0.10	0.56	0.185	0.104
0.06	0.60	0.200	0.107
0.03	0.63	0.205	0.116
0.00	0.66	0.215	0.122
-0.05	0.71	0.235	0.133
-0.10	0.76	0.250	0.140
-0.14	0.80	0.255	0.144
-0.20	0.86	0.265	0.150
-0.30	0.96	0.280	0.158
-0.40	1.06	0.295	0.167
-0.50	1.16	0.310	0.175
-0.60	1.26	0.320	0.181
-0.70	1.36	0.340	0.192
-0.80	1.46	0.350	0.198

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE IX

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 1 N H<sub>2</sub>SO<sub>4</sub> (pH = 0.38) AT 25°C (RUN 2)

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp.cm <sup>-2</sup>
0.38	0.27	0.000	0.000
0.36	0.29	0.001	0.0056
0.33	0.32	0.009	0.0051
0.29	0.36	0.0435	0.0252
0.25	0.40	0.120	0.068
0.21	0.44	0.140	0.079
0.15	0.50	0.170	0.096
0.09	0.56	0.180	0.102
0.00	0.65	0.200	0.113
-0.12	0.77	0.205	0.116
-0.24	0.89	0.215	0.117
-0.36	1.01	0.230	0.130
-0.48	1.13	0.245	0.134
-0.60	1.25	0.245	0.139
-0.72	1.37	0.250	0.142
-0.84	1.49	0.255	0.150
-1.20	1.85	0.265	0.150
-1.50	2.15	0.280	0.158
-2.00	2.65	0.280	0.158
-2.50	3.15	0.300	0.172

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE X

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
 OF TUNGSTEN IN 0.24 N  $\text{H}_2\text{SO}_4$ +0.76 N  $\text{K}_2\text{SO}_4$   
 (pH = 1.5) AT 25°C

Potential		Current	Current Density
			$\times 10^3$
volts (NSE)	volts (SHE)	ma	amp $\cdot$ cm $^{-2}$
0.43	0.23	0.0000	0.0000
0.42	0.25	0.0015	0.00085
0.40	0.26	0.0025	0.00142
0.39	0.28	0.0040	0.00228
0.37	0.30	0.0070	0.00398
0.35	0.32	0.0125	0.0071
0.33	0.33	0.0180	0.0100
0.32	0.35	0.0240	0.0146
0.30	0.37	0.0275	0.0156
0.28	0.39	0.0300	0.0170
0.25	0.42	0.0300	0.0170
0.21	0.46	0.0330	0.0187
0.16	0.51	0.0370	0.0210
0.11	0.56	0.0420	0.0238
0.06	0.61	0.0430	0.0250
0.00	0.67	0.0430	0.0250
-0.10	0.77	0.0400	0.0226
-0.20	0.87	0.0430	0.0250
-0.40	1.07	0.0430	0.0250
-0.70	1.37	0.0430	0.0250
-1.20	1.87	0.0450	0.0256
-1.83	2.50	0.0450	0.0256
-2.50	3.17	0.0450	0.0256
-3.00	3.67	0.0450	0.0256

Area of the electrode = 1.76 cm $^2$

TABLE XI

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
 OF TUNGSTEN IN 0.1 N H<sub>2</sub>SO<sub>4</sub>+0.9 N K<sub>2</sub>SO<sub>4</sub>  
 (pH = 2.5) AT 25°C

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.46	0.21	0.000	0.000
0.43	0.24	0.003	0.0017
0.41	0.26	0.005	0.003
0.39	0.28	0.008	0.0045
0.37	0.30	0.012	0.0068
0.35	0.32	0.0175	0.010
0.32	0.35	0.026	0.015
0.29	0.38	0.030	0.017
0.23	0.44	0.0325	0.0185
0.13	0.54	0.040	0.023
0.00	0.67	0.048	0.027
-0.50	1.17	0.049	0.028
-1.00	1.67	0.050	0.0285
-1.50	2.17	0.050	0.0285
-2.00	2.67	0.050	0.0285
-2.50	3.17	0.050	0.0285
-3.00	3.67	0.050	0.0285

Area of the electrode = 1.76 cm<sup>2</sup>



TABLE XII

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 1 N  $K_2CO_3$  (pH = 11.5) AT 25°C

Potential		Current	Current Density $\times 10^3$
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.66	-0.38	0.000	0.000
0.64	-0.36	0.03	0.013
0.62	-0.34	0.04	0.023
0.60	-0.32	0.09	0.051
0.585	-0.305	0.13	0.074
0.57	-0.29	0.21	0.120
0.555	-0.275	0.54	0.306
0.54	-0.26	0.51	0.290
0.52	-0.24	0.86	0.430
0.50	-0.22	1.48	1.840
0.48	-0.20	3.00	1.700
0.46	-0.18	3.30	1.88
0.43	-0.15	4.20	2.45
0.40	-0.12	5.40	3.10
0.37	-0.09	6.80	3.80
0.34	-0.06	9.90	5.60
0.31	-0.03	18.0	10.2
0.26	+0.02	32.0	18.0
0.21	+0.07	50.0	29.0

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE XIII

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 0.1 N KOH+0.9 N K<sub>2</sub>SO<sub>4</sub> (pH = 12.7) AT 25°C

Potential		Current	Current Density x 10 <sup>3</sup>
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.69	-0.41	0.000	0.000
0.67	-0.39	0.0085	0.005
0.65	-0.37	0.020	0.0113
0.63	-0.35	0.040	0.0226
0.61	-0.33	0.080	0.0455
0.59	-0.31	0.180	0.102
0.57	-0.29	0.500	0.284
0.55	-0.27	0.900	0.520
0.53	-0.25	2.70	1.50
0.51	-0.23	4.60	2.60
0.49	-0.21	5.80	3.30
0.45	-0.17	7.40	4.20
0.41	-0.13	11.0	6.8
0.37	-0.09	16.0	9.0
0.32	-0.04	22.0	12.5
0.28	0.00	26.0	14.7
0.23	0.05	27.0	15.0

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE XIV

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 1 N KOH (pH = 13.6) AT 25°C

Potential		Current	Current Density $\times 10^3$
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.70	-0.42	0.000	0.000
0.68	-0.40	0.016	0.009
0.665	-0.385	0.033	0.0188
0.65	-0.37	0.052	0.0295
0.63	-0.35	0.110	0.057
0.615	-0.335	0.250	0.15
0.60	-0.32	0.620	0.34
0.57	-0.29	1.25	0.70
0.54	-0.26	2.40	1.35
0.49	-0.21	8.60	3.80
0.46	-0.18	13.5	7.70
0.43	-0.15	24.0	13.0
0.39	-0.11	42.0	24.0
0.36	-0.08	57.0	32.0
0.31	-0.03	89.0	50.0

Area of the electrode = 1.76 cm<sup>2</sup>

TABLE XV

CURRENT-POTENTIAL DATA FOR THE ANODIC DISSOLUTION  
OF TUNGSTEN IN 3 N KOH (pH = 14.5) AT 25°C

Potential		Current	Current Density $\times 10^3$
volts (NSE)	volts (SHE)	ma	amp·cm <sup>-2</sup>
0.75	-0.47	0.000	0.000
0.73	-0.45	0.008	0.0045
0.715	-0.435	0.016	0.0091
0.70	-0.42	0.028	0.016
0.68	-0.40	0.062	0.035
0.66	-0.38	0.130	0.075
0.64	-0.36	0.380	0.216
0.62	-0.34	0.640	0.358
0.60	-0.32	0.900	0.515
0.57	-0.29	2.20	1.24
0.53	-0.25	11.0	6.25
0.50	-0.22	30.0	17.0
0.47	-0.19	78.0	44.0
0.43	-0.15	200	113
0.40	-0.12	300	170

Area of the electrode = 1.76 cm<sup>2</sup>

## APPENDIX E

## Thermodynamic Data

TABLE XVI

STANDARD FREE ENERGIES OF REACTION FOR VARIOUS  
METAL OXIDES AND WATER \*

Reaction	$\Delta G_{298}^{\circ}, \text{Kcal}$
1. $\text{HgO} + \text{H}_2\text{O} = \text{Hg}(\text{OH})_2$	-66.0 - (-13.9-56.7) = +4.6
2. $\text{MnO} + \text{H}_2\text{O} = \text{Mn}(\text{OH})_2$	-145.9 - (-86.8-56.7) = -2.4
3. $\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$	-199.3 - (-136.1-56.7) = -6.5
4. $\text{PbO} + \text{H}_2\text{O} = \text{Pb}(\text{OH})_2$	-100.6 - (-45.2-56.7) = +1.3
5. $\text{FeO} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2$	-115.6 - (-58.4-56.7) = -0.5
6. $\text{CoO} + \text{H}_2\text{O} = \text{Co}(\text{OH})_2$	-108.9 - (-51.0-56.7) = -1.2
7. $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$	-214.3 - (-144.4-56.7) = -13.2
8. $\text{CdO} + \text{H}_2\text{O} = \text{Cd}(\text{OH})_2$	-112.5 - (-53.8-56.7) = -2.0
9. $\text{NiO} + \text{H}_2\text{O} = \text{Ni}(\text{OH})_2$	-108.3 - (-51.7-56.7) = +0.1
10. $\text{TeO}_2 + \text{H}_2\text{O} = \text{H}_2\text{TeO}_3$	-115.7 - (-64.6-56.7) = +5.6
11. $\text{SnO} + \text{H}_2\text{O} = \text{Sn}(\text{OH})_2$	-117.6 - (-61.5-56.7) = -0.6
12. $\text{TiO}_2 + \text{H}_2\text{O} = \text{TiO}_2 \cdot \text{H}_2\text{O}$	-253.0 - (-212.3-56.7) = +16.0
13. $\text{ZrO}_2 + \text{H}_2\text{O} = \text{ZrO}_2 \cdot \text{H}_2\text{O}$	-311.5 - (-247.7-56.7) = -7.1
14. $\text{HfO}_2 + \text{H}_2\text{O} = \text{HfO}_2 \cdot \text{H}_2\text{O}$	-325.5 - (-252.2-56.7) = -16.6
15. $\text{CrO}_3 + \text{H}_2\text{O} = \text{H}_2\text{CrO}_3$	-185.9 - (-120.0-56.7) = -9.2
16. $\text{MoO}_3 + \text{H}_2\text{O} = \text{H}_2\text{MoO}_3$	-227.0 - (-161.9-56.7) = -0.4
17. $\text{ZnO} + \text{H}_2\text{O} = \text{Zn}(\text{OH})_2$	-131.8 - (-75.1-56.7) = 0
18. $\text{GeO}_2 + \text{H}_2\text{O} = \text{H}_2\text{GeO}_3$	-186.8 - (-136.1-56.7) = +6.0
19. $\text{OsO}_4 + \text{H}_2\text{O} = \text{H}_2\text{OsO}_5$	-126.6 - (-70.7-56.7) = +0.8
20. $\text{SiO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SiO}_3$	-242.0 - (-190.9-56.7) = +5.6
21. $\text{CuO} + \text{H}_2\text{O} = \text{Cu}(\text{OH})_2$	-85.3 - (-30.4-56.7) = +1.8
22. $\text{PdO} + \text{H}_2\text{O} = \text{Pd}(\text{OH})_2$	-72.0 - (-14.4-56.7) = -0.9
23. $\text{RuO}_4 + \text{H}_2\text{O} = \text{H}_2\text{RuO}_5$	-81.6 - (-26.1-56.7) = +1.1

\*References 7 and 10

## VITA

Ching-lun Wu was born on April 17, 1936, in Taiwan, China. He graduated from high school in 1954. He entered the Tunghai University and graduated with a B.S. degree in Chemical Engineering in June, 1959.

After graduation, he served in the Chinese Army for a period of one and a half years and was assigned as a second lieutenant. He worked for the Taiwan Alkali Company, Kaihsiung Plant for nine years after military service.

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