[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarography of the Various Oxidation States of Tungsten

BY JAMES J. LINGANE AND LYNDON A. SMALL

The polarography of +6 tungsten in weakly acid solution and of the heteropoly acids, such as the phospho- and silico-tungstates has been studied by Souchay.[1] Stackelberg, *et al.*,[2] studied the polarography of tungsten(VI) in concentrated hydrochloric acid and they reported only a single reduction wave. No polarographic studies of tungsten in oxidation states lower than +6 have previously been reported.

No polarographic waves are found for tungsten (VI) in basic or neutral solution. Tungsten(VI) is insoluble in dilute strong acids, but is soluble in concentrated halogen acids. This paper presents the results of an investigation of the polarography of the various oxidation states of tungsten in hydrochloric acid, together with application of controlled potential electrolysis to the interpretation of the polarograms and the preparation of the lower oxidation states.

Experimental

Standard solutions of tungsten(VI) were prepared from reagent quality sodium tungstate and standardized gravimetrically by the conventional tungstic acid precipitation with the aid of cinchonine.[3]

Polarographic measurements were made both by the resistance–potentiometer method,[4] and by use of a Heyrovsky–Shikata type photographic recording polarograph constructed in this Laboratory. An H-type cell[5] was used in most cases, with a saturated calomel electrode. Nitrogen, hydrogen or carbon dioxide purified by passage over copper gauze at 400°, or by passage through a solution of a chromous salt, was used for removal of dissolved oxygen and protection of air-sensitive solutions. All polarographic measurements were made at 25.0°; and all potentials are referred to the saturated calomel electrode at 25°. Appropriate corrections for residual current were made in calculating diffusion current constants. Electrolytic reductions at controlled potential were carried out according to the technique of Lingane, Swain and Fields,[6] with a cell of the same design as that used by those authors but with the rubber stopper replaced by a ground-glass joint and cap. The cell was constructed from a 250-ml. wide-mouth Erlenmeyer flask, with a 30-mm. medium porosity Pyrex sintered-glass disk as diaphragm. A mercury cathode and carbon anode were used. The potential of the mercury electrode was automatically controlled by a potentiostat[7] with respect to a saturated calomel reference electrode. Reduced solutions in the cell were protected by nitrogen or hydrogen, which was passed over rather than through the solution. Polarographic measurements on the cell contents were made by inserting the dropping electrode into the cell and using the mercury pool as anode.

Oxidation states were determined both by measurement with an oxygen–hydrogen coulometer of the current passed during reduction[8] and by an iodate titration. The latter was based on the Andrews iodine monochloride procedure.[9] According to Lang[10] iodate ion directly oxidizes tungsten (III) to tungsten(VI) only slowly, but reacts rapidly if catalyzed by ferric iron. Accordingly, an aliquot of the reduced solution was added to an air-free solution of excess of ferric iron in 4 to 6 *M* hydrochloric acid, and the ferrous iron produced was titrated potentiometrically with standard 0.01 *N* potassium iodate solution. The validity of this method was established by titration of samples of tungsten(III) prepared by reduction of tungsten(VI) in 12 *M* hydrochloric acid by saturated lead amalgam by the method of Someya.[11] Accuracy of about ±0.5% was obtained with 0.1 *N* iodate solutions. Deduction of a small blank (*ca.* 0.10 ml.) was found necessary in titrating with 0.01 *N* iodate.

Absorption spectra were recorded by use of the Beckman Model DU Photoelectric Quartz Spectrophotometer, with 1-cm. quartz cells. Some measure of protection of the solutions from air and of protection of the instrument from acid fumes was obtained by sealing the loose fitting glass cell covers with vaseline, and by providing the cell compartment with a cover fitted with tubulatures through which air was passed to provide ventilation. Slit widths of 0.02 to 0.2 mm. were used, corresponding to nominal band widths smaller than 5 millimicrons.

Results and Discussion

Tungsten(VI).—It was found that tungsten (VI) in 12 *M* hydrochloric acid produces a double polarographic wave as shown in Fig. 1, one wave starting from zero applied e. m. f. and the second having a half-wave potential of −0.56 v. *vs.* S.C.E. In less concentrated acid, the half-

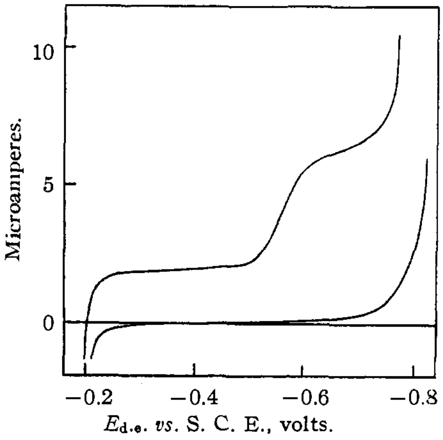

Fig. 1.—Polarogram of 1.00 millimolar tungsten(VI) in 12 *M* hydrochloric acid.

---

[1] P. Souchay, *Ann. chim.*, **18**, 61 (1943); **18**, 73 (1943); **18**, 169 (1943); **19**, 102 (1944); **20**, 73 (1945); **20**, 96 (1945); **1**, 232 (1946).

[2] M. v. Stackelberg, P. Klinger, W. Koch and E. Krath, *Forschungsberichte Tech. Mitt. Krupp, Essen*, **2**, 59 (1939).

[3] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1942.

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[5] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[6] J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943).

[7] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945);

[8] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

[9] L. W. Andrews, *ibid.*, **25**, 756 (1903).

[10] Oesper, "Newer Methods of Volumetric Analysis," D. Van Nostrand Co., New York, N. Y., 1938.

[11] K. Someya, *Z. anorg. allgem. Chem.*, **145**, 168 (1925).

wave potential of the second wave is shifted somewhat in the negative direction. In both 10 *M* and 8 *M* hydrochloric acid, the half-wave potential was −0.62 v.; in 6 *M* acid −0.64 v.; in 4 *M* acid −0.66 v. *vs.* S.C.E. The solubility of tungsten (VI) in hydrochloric acid much less concentrated than 4 *M* is too small to allow the wave to be distinguished. Diffusion current constant data are given in Table I.

TABLE I

DIFFUSION CURRENT CONSTANTS OF TUNGSTEN(VI) IN HYDROCHLORIC ACID AT 25.0°

(a) 12 *M* Hydrochloric Acid. $m^{2/3}t^{1/6}$ = 1.61 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.40 v. and 1.63 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.67 v. *vs.* S. C. E.

Tungsten(VI) millimolar	$i_d/Cm^{2/3}t^{1/6}$ at −0.40 v.	at −0.67 v.
1.49	1.29	3.82
2.44	1.32	3.84
3.79	1.31	3.80
4.65	1.32	..
Av.	1.31 ± 1	3.82 ± 2

(b) 10 *M* Hydrochloric Acid. $m^{2/3}t^{1/6}$ = 1.56 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.40 v. and 1.59 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.75 v. *vs.* S. C. E.

Tungsten(VI) millimolar	$i_d/Cm^{2/3}t^{1/6}$ at −0.40 v.	at −0.75 v.
1.00	1.42	4.35
1.97	1.42	4.32

(c) 8 *M* Hydrochloric Acid. $m^{2/3}t^{1/6}$ values as in (b)

Tungsten(VI) millimolar	$i_d/Cm^{2/3}t^{1/6}$ at −0.40 v.	at −0.75 v.
1.00	1.49	4.78
1.97	1.45	4.62

Since the ratio of the diffusion current constants is 1:3, reduction apparently proceeds to the +5 and +3 states, respectively. The alternative would be deposition of tungsten metal, which has never been achieved from such strongly acid solutions. Direct proof of the above interpretation is given below.

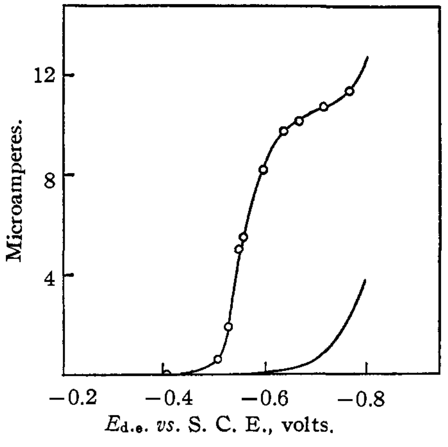

Fig. 2.—Polarogram of 2.61 millimolar tungsten(V) in 12 *M* hydrochloric acid.

Tungsten(V).—Reduction of solutions of tungsten(VI) in 12 *M* hydrochloric acid on the mercury cathode at −0.40 v. *vs.* S.C.E., *i. e.*, corresponding to the plateau of the first wave of the tungsten(VI) polarogram, produced blue solutions of tungsten(V). The identity of the product was established both by titration with iodate, which indicated an oxidation state of 5.00 in a typical case, and coulometric measurements during the controlled potential electrolysis, which indicated an oxidation state of 4.97. The +5 state has been obtained previously by Collenberg and Backer[12] by reduction of tungsten(VI) in concentrated hydrochloric acid on a platinum cathode without potential control.

As shown in a previous paper[13] the current in a controlled potential electrolysis in which diffusion is the controlling factor obeys the relation $i = i_0 \cdot 10^{-kt}$, where $k = 0.43\ DA/\delta V$, where D is the diffusion coefficient, A the electrode area, V the solution volume, δ the diffusion layer thickness and t is time. In reductions of 2, 4 and 8 millimolar tungsten(VI) in 12 *M* hydrochloric acid at −0.40 v. *vs.* S.C.E., the plots of log i *vs.* time gave straight lines as required by the above equation, and the values of k obtained were 0.049, 0.052 and 0.052 min.$^{-1}$, respectively. Under these conditions reduction to the +5 state was 99% complete in 2/0.051 or thirty-nine minutes.

The polarogram for the reduction of tungsten(V) to the +3 state is shown in Fig. 2. The slope of the wave corresponds to a reversible 2-electron reduction. The half-wave potential (0.56 v.) is identical with that of the second wave of the tungsten(VI) polarogram, and the diffusion current constant as shown in Table II agrees very well with the value 2.51 found for the difference between the two constants for the tungsten(VI) waves. No anodic wave is observed, showing that the potential of the tungsten(VI)-tungsten(V) couple has a value more positive than the oxidation potential of mercury.

TABLE II

DIFFUSION CURRENT CONSTANT OF TUNGSTEN(V) IN 12 *M* HYDROCHLORIC ACID AT 25°

Tungsten(V) millimolar	$m^{2/3}t^{1/6}$ mg.$^{2/3}$ sec.$^{-1/2}$	$i_d/Cm^{2/3}t^{1/6}$ at −0.67 v. *vs.* S. C. E.
0.79	1.57	2.53
1.59	1.59	2.55
1.78	2.09	2.53
2.37	1.57	2.49
	Av.	2.53 ± 2

On dilution of a hydrochloric acid solution of tungsten(V) the blue color remains and the polarogram is qualitatively unchanged until the acid concentration is somewhat less than 6 *M*, but on further dilution the solution turns progressively more yellow, and the polarographic wave disappears.

---

[12] O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924).

[13] J. J. Lingane, *Anal. Chim. Acta*, **2**, in press (1948).

Coulometric Reduction of Tungsten(V).—The formation of tungsten(IV) in the reduction of tungsten in hydrochloric acid has previously been somewhat uncertain. The solid $K_2W(OH)Cl_5$ was isolated by Collenberg and Backer[12] from solutions of tungsten in concentrated hydrochloric acid after reduction on lead or mercury cathodes to below the +5 state, but these authors voiced the suspicion that the apparent tungsten(IV) might be only a compound between tungsten(V) and tungsten(III). The tungsten(VI) and tungsten(V) polarograms that we have studied indicate that reduction of tungsten(V) to tungsten(III) takes place directly, and that tungsten(IV) is unstable with respect to disproportionation into the higher and lower states.

Collenberg and Backer[12] isolated red $Rb_2WCl_5 \cdot H_2O$ containing tungsten(III) from solutions reduced on a mercury or lead cathode at temperatures below 18°; the red form was converted to the familiar green $Rb_3W_2Cl_9$ at higher temperatures.

In order to carry out the reaction corresponding to the tungsten(V) polarogram in Fig. 2, a solution of tungsten(VI) in 12 *M* hydrochloric acid was first reduced to tungsten(V) at −0.40 v. and then reduced further at −0.67 v. *vs.* S.C.E., a potential on the plateau of the tungsten(V) wave. The blue tungsten(V) solution first became purple, then red and finally yellow. After passing the +5 state and while the solution remained red the current consumption indicated by the coulometer was in close agreement with that indicated by iodate titration, *i. e.*, the current efficiency was 100%. The indicated oxidation state at one such point in the reduction of 0.01 *M* tungsten at 18° was 3.08 coulometrically and 3.09 by iodate titration. Since the solution was still red at this point, and turned yellow rather rapidly after the current had dropped to a nearly negligible value, it is clear that the red solution contained tungsten(III) rather than tungsten(IV). Immediately after completion of the electrolysis, iodate titration of the yellow solution indicated an oxidation state of 2.89, while the coulometer indicated 2.76. The latter value was lower due to a visible simultaneous reduction of a small amount of hydrogen ion near the end of the electrolysis. About fifteen minutes after completion, iodate titration indicated an oxidation state of 3.01. It thus appears possible that some lower state is formed, but is rapidly oxidized by hydrogen ion to the +3 state. All attempts to obtain reduction to a lower state failed. It is seen, therefore, that the reduction of tungsten(V) proceeds to red tungsten(III), which is spontaneously converted to the green or yellow form. The red form is presumably the reduction product involved in the polarographic wave.

We have obtained some evidence that either tungsten(IV) or a compound of tungsten(V) and tungsten(III) is produced transiently during the coulometric reduction of hydrochloric acid solutions of tungsten(V) when the concentration of the latter is relatively large. When 8 and 2 millimolar solutions of tungsten(V) were reduced, the red color produced after the quantity of electricity passed corresponded to the +4 state was much more intense with the larger concentration than could be accounted for by the ratio of the concentrations. Such intensification of color is commonly associated with compounds containing an element in two oxidation states. Further indication of an apparent +4 state was obtained by measurement of the oxidation potential at various stages during the reduction of a 2 millimolar and an 8 millimolar solution of tungsten(V). The potentials were measured against the saturated calomel electrode by interrupting the electrolysis and employing the large mercury cathode as indicator electrode. The data obtained are shown in Table III.

TABLE III

POTENTIAL CHANGES DURING REDUCTION OF TUNGSTEN (V) TO RED TUNGSTEN(III) IN 12 *M* HYDROCHLORIC ACID

The potentials are referred to the saturated calomel electrode.

(a) Total tungsten, 2.00 milimolar; 1 electron = 8.40 ml. hydrogen-oxygen at S. T. P.

Coulometer reading, S.T.P., ml.	Apparent oxidation state	$E_{obs.}$	E^0
0	5.00	−0.350	.....
2.50	4.70	− .537	−0.559
4.23	4.50	− .541	− .555
6.44	4.23	− .549	− .555
8.43	4.00	− .554	− .554
10.80	3.71	− .562	− .555
12.50	3.51	− .568	− .554
13.81	3.35	− .575	− .555
15.01	3.21	− .583	− .555
16.10	3.08	− .595	− .554[a]
16.65	3.02	− .606	− .556[a]
		Av.	−0.555 ± 1

[a] These solutions were beginning to turn yellow.

(b) Total tungsten, 8.00 millimolar; 1 electron = 33.6 ml. S. T. P.

0	5.00	−0.343	.....
3.38	4.90	− .495	− .533
9.95	4.70	− .504	− .526
15.91	4.53	− .505	− .520
21.25	4.37	− .513	− .523
27.80	4.17	− .502	− .506
35.8	3.92	− .516	− .514
44.4	3.68	− .533	− .524

The values of E^0 listed in the last column of Table III were computed by the equation $E_{obs.} = E^0 - (0.059/2) \log C_{III}/C_V$, where C_{III}/C_V is the ratio of the concentrations of +3 and +5 tungsten calculated from the coulometer readings. With the 2 millimolar solution a very constant value of E^0 is obtained over the entire range of values of C_{III}/C_V, showing that the couple behaves reversibly at this concentration. Furthermore the E^0 value agrees with the half-wave potential observed with tungsten(V) solutions (−0.56 v.), showing that the reduction of tungsten(V) to red tungsten(III) proceeds reversibly at the dropping electrode. With the 8 millimolar solution, on the other hand, the E^0 values are much too positive, and are not constant with varying values of C_{III}/C_V but show a steady decrease down to an apparent oxidation state of +4, and then an increase with larger values of the C_{III}/C_V ratio. Furthermore the observed potentials with the 8 millimolar solution were not steady but showed a continuous positive drift. Slow combination of tungsten(V) and tungsten(III) to produce a compound of the two states, or actual reaction to produce tungsten(IV), could account for this behavior.

Red Tungsten(III).—Solutions of the red form of tungsten(III) in 12 M hydrochloric acid were prepared by partial electrolytic reduction of tungsten(V) as described above. The reductions were not carried to completion because transformation of the red tungsten(III) to the yellow form occurs when this is done. The typical polarogram of such a mixture shown in Fig. 3 displays a well developed anodic diffusion current due to the oxidation of tungsten(III), as well as the cathodic wave of the remaining tungsten(V).

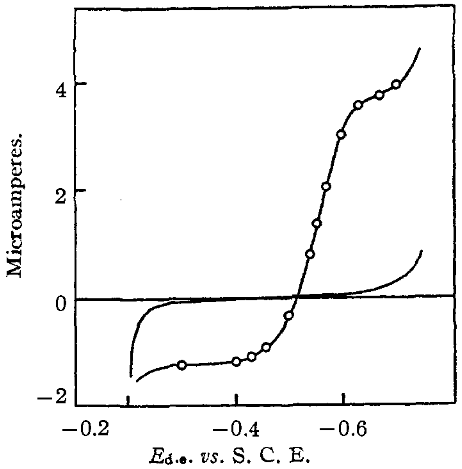

Fig. 3.—Polarogram of a mixture of 0.91 millimolar tungsten(V) and 0.67 millimolar red tungsten(III) in 12 M hydrochloric acid.

The fact that the composite cathodic–anodic wave shows no inflection at zero current is a commonly accepted criterion for reversibility of the electrode reactions but is misleading in this case because the anodic reaction is not the reverse of the cathodic reaction.

The anodic wave of red tungsten(III) actually corresponds to oxidation to the +4 state and not to the +5 state. With concentrations of red tungsten(III) between 0.3 and 0.7 millimolar the anodic diffusion current was directly proportional to concentration, and the average value of the diffusion current constant $i_d/Cm^{2/3}t^{1/6}$ was 1.10 ± 0.01 at 25° in 12 M hydrochloric acid. This is somewhat less than one-half the diffusion current constant (2.53) observed in the 2-electron reduction of tungsten(V), and slightly smaller than the diffusion current constant (1.31) observed in the 1-electron reduction of tungsten(VI) in 12 M hydrochloric acid. It is evident that the red tungsten(III) undergoes only a 1-electron oxidation to the +4 state. The alternative conclusion (oxidation to the +5 state) would require that the diffusion coefficient of tungsten(III) be about five times smaller than the diffusion coefficients of tungsten(V) and tungsten(VI), and this is very improbable.

This interesting result indicates that the rate of disproportionation of tungsten(IV) must be so small that no appreciable disproportionation occurs during the life of each mercury drop at the dropping electrode.

The absorption spectrum of red tungsten(III), which has not previously been reported, is shown as curve 1 in Fig. 4. This was obtained with a mixture of tungsten(III) and tungsten(V) and correction was applied for the small contribution of tungsten(V) to the measured optical density in calculating the extinction coefficient of the tungsten(III).

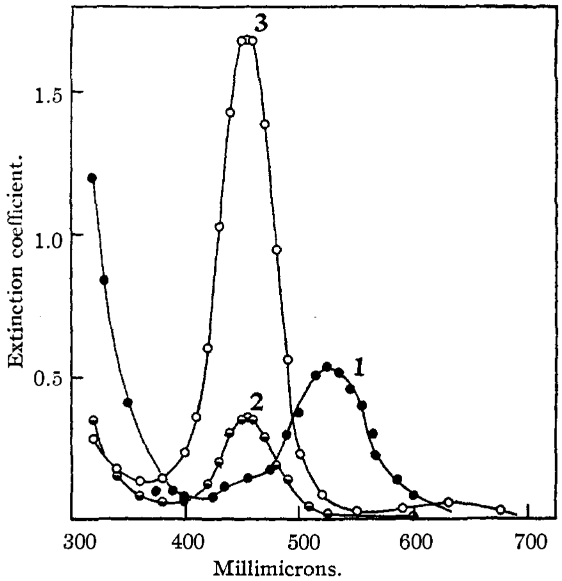

Fig. 4.—Absorption spectra of tungsten(III): (1), red form; (2), yellow form; (3), green form. Measured with Beckman UV Spectrophotometer with slit widths adjusted so that nominal band width was smaller than 4 millimicrons at all wave lengths.

Yellow and Green Tungsten(III).—Solutions of the red tungsten(III) turn yellow on standing, continued electrolysis or heating. A typical polarogram of the previously unreported yellow tungsten(III) is shown in Fig. 5. The well developed anodic wave has a half-wave potential of −0.53 v. vs. S.C.E., and thus nearly the same as that of the red form. The anodic diffusion current is directly proportional to the concentration of yellow tungsten(III) only below about 4 millimolar, and with larger concentrations the diffusion current "constant" decreases significantly. The average value of $i_d/Cm^{2/3}t^{1/6}$ with 1 to 4 millimolar yellow tungsten(III) in 12 *M* hydrochloric acid was found to be 1.38 = 0.06 at 25°. This is so nearly the same as that observed with red tungsten(III) that it is clear that the yellow form, like the red form, is oxidized only to the +4 state at the dropping electrode.

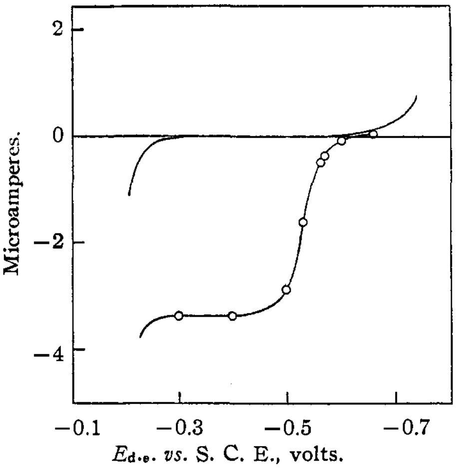

Fig. 5.—Polarogram of 1.59 millimolar yellow tungsten (III) in 12 *M* hydrochloric acid.

That the "yellow" form of tungsten(III) is actually distinct from the familiar "green" modification is demonstrated by the fact that solutions of the green $K_3W_2Cl_9$, prepared by the method of Olsson,[14] showed no anodic wave in either concentrated or dilute hydrochloric acid.

Absorption spectra of the "yellow" and "green" forms of tungsten(III) are shown in Fig. 4. The extinction of the green form at 455 millimicrons was found to obey Beer's law over a tenfold range of concentrations. The spectrum of the "yellow" form shows the same band at 455 millimicrons as the green form, but its extinction coefficient is very much smaller. Furthermore, solutions of the "yellow" form do not obey Beer's law; the extinction coefficient at 455 millimicrons was found to increase from 0.058 to 0.71 when the concentration was increased from 1 to 16 millimolar. The extinction coefficient of the green form is 1.64 at 455 millimicrons.

It seems very likely from these experiments that the "yellow" form may actually be a colorless modification of tungsten(III), and the apparent yellow color probably is caused by a small amount of the "green" form in the solutions used. This yellow or colorless form transforms to the "green" form, the rate and relative proportion of the "green" form increasing with increasing concentration.

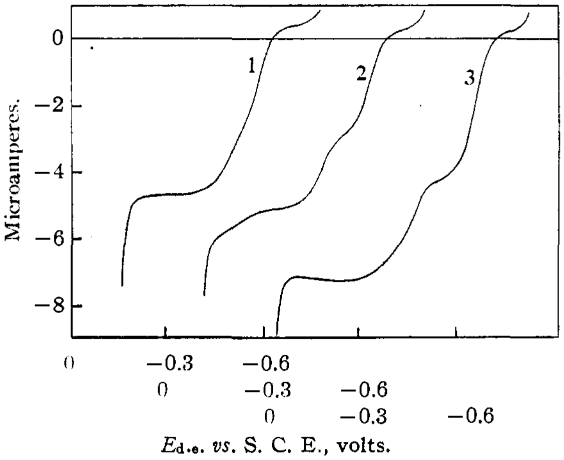

Fig. 6.—Polarogram of 1.33 millimolar yellow tungsten (III) in: (1) 9 *M*, (2) 6 *M*, and (3) 3 *M* hydrochloric acid.

Figure 6 shows polarograms of the same concentration of the "yellow" tungsten(III) in 9, 6 and 3 *M* hydrochloric acid. With decreasing concentration of hydrochloric acid the anodic wave divides into two parts and the total diffusion current increases markedly. The magnitude of the total diffusion current in 3 *M* hydrochloric acid, coupled with the fact that the two parts of the wave are of nearly equal height, indicates stepwise oxidation of the tungsten(III) to the +4 and +5 states. The other alternative is that the doublet wave results from the separate oxidation to the +4 state of two different molecular species of +3 tungsten in sluggish equilibrium, and the increase in the total diffusion current would then be attributed to an increased diffusion coefficient in 3 *M* hydrochloric acid. We believe, however, that this is unlikely.

Controlled Potential Oxidation of "Yellow" Tungsten(III).—Electrolytic oxidation of yellow solutions of tungsten(III) in 12 *M* hydrochloric acid was performed with the potential of the mercury electrode at −0.40 v. *vs.* S C.E., corresponding to the plateau of the anodic polarographic wave (compare Fig. 5). The oxidation was followed coulometrically. The results obtained with various concentrations of tungsten (III) at different temperatures are summarized in Table IV.

In all cases the current decreased to virtually zero at the end of the electrolysis, and the values of the average final oxidation state computed from the coulometer reading are listed in Table IV.

During the initial stages of the electrolysis the solutions tended to bleach slightly. For example, during the oxidation of a 4 millimolar solution the optical density at 455 millimicrons decreased from 0.197 to 0.186, and no other absorption band appeared, up to an apparent oxidation state of 3.50. On continued electrolysis

---

[14] O. Olsson, *Z. anorg. allgem. Chem.*, **88**, 50 (1914).

TABLE IV

FINAL OXIDATION STATE OF YELLOW TUNGSTEN(III) OXIDIZED AT −0.40 V. *vs.* S. C. E. IN 12 *M* HYDROCHLORIC ACID

Oxidation states determined by coulometric measurement.

Tungsten, mg. atoms/l.	Temp. of oxidation, °C.	Oxidation state, av.
1.00	25	4.49
2.00	10	4.48
2.00	25	4.56
2.00	25	4.64
2.00	30	4.52
4.00	12	4.80
4.00	20	4.51
4.00	20	4.48
4.00	20	4.65
4.00	25	4.76
4.00	25	4.70
4.00	30	4.20
4.00	30	4.37
8.00	13	3.99
8.00	12	4.08
8.00	20	4.37
8.00	20	4.38
8.00	25	4.35
8.00	25	4.33
8.00	33	4.12
16.0	25	3.86

the solution became red and the absorption band at 525 millimicrons of red tungsten(III) appeared. This band then faded out and the solution finally acquired a pale brownish-yellow color with a weak band at 455 millimicrons.

With the larger concentrations of tungsten (III) the final oxidation state is very close to +4, especially at the lower temperatures, but with small concentrations the final apparent oxidation state is consistently in the neighborhood of 4.5 and independent of the temperature between 10 and 30°.

These results furnish a clear indication that a fairly stable molecular species containing tungsten (IV) and tungsten(V) in a 1:1 ratio is formed in the more dilute solutions. Apparently the "yellow" tungsten(III) is first oxidized to a colorless species of tungsten(IV), which then slowly disproportionates to red tungsten(III) and tungsten(V). On continued electrolysis the red tungsten(III) is oxidized to tungsten (IV), and finally the tungsten(IV) and tungsten (V) combine to form a stable species with an apparent oxidation state of +4.5. The fact that with the larger concentrations the final oxidation state was closer to +4 than +4.5 was simply caused by the original presence in these solutions of a considerable proportion of the green tungsten(III) which, as the polarographic experiments demonstrate, is not easily oxidized at the mercury electrode. This interpretation is substantiated by the fact that the absorption spectra of the final solutions obtained with the larger concentrations showed the characteristic band of green tungsten(III) at 455 millimicrons. No other band is observed with the final solutions.

The final solutions containing the tungsten in an apparent oxidation state of +4.5 produce a polarogram which comprises a single cathodic wave with a half-wave potential of −0.56 v. *vs.* S.C.E., and is thus very similar to the wave of tungsten(V). The average diffusion current constant, measured with several solutions in which the apparent oxidation state of the tungsten was between 4.49 and 4.56, was 2.28 ± 0.04, which is consistent with reduction to the +3 state. This was confirmed by controlled potential reductions of the final solutions which yielded the "yellow" form of tungsten(III).

Summary

The polarogram of tungsten(VI) in 12 *M* hydrochloric acid consists of two waves: one, reduction to tungsten(V), starting from the anodic dissolution potential of mercury, and the second, reduction to red tungsten(III), having a half-wave potential of −0.56 v. *vs.* S.C.E. Using these waves as guides, tungsten(VI) was reduced by controlled potential electrolysis with a large mercury cathode at −0.40 v. *vs.* S.C.E. to tungsten(V), the polarogram of which is identical with the second wave of the tungsten(VI) polarogram.

On reducing tungsten(V) at −0.67 v. *vs.* S.C.E. red tungsten(III) was found to be the primary product, with a deep red tungsten(IV) formed during reduction of 4 and 8 millimolar solutions but not of 2 millimolar. A mixture of tungsten(V) and red tungsten(III) gives a continuous anodic–cathodic polarographic wave at −0.55 v., with the anodic oxidation being to tungsten(IV) rather than to tungsten(V).

The standard reduction potential of the tungsten(V), red tungsten(III) couple in 12 *M* hydrochloric acid at 25° was found to be −0.555 ±5 v. *vs.* S.C.E.

Red tungsten(III) is spontaneously converted to a "yellow" tungsten (III) which displays an anodic polarographic wave at −0.53 v. *vs.* S.C.E. It was shown that in more concentrated solution, the familiar green tungsten (III), which gives no polarographic wave, is formed.

Electrolytic oxidation of yellow tungsten(III) at −0.40 v. *vs.* S.C.E. produced tungsten(IV) which disproportionates to red tungsten(III) and tungsten(V); tungsten(V) and tungsten (IV) then combine in dilute solution in a 1:1 ratio to form a species with an apparent oxidation state of +4.5. The polarogram of this species shows a cathodic wave at −0.56 v. *vs.* S.C.E., corresponding to reduction to the +3 state.

Absorption spectra of the red, yellow and green species of tungsten(III) are presented.

CAMBRIDGE 38, MASS. RECEIVED OCTOBER 26, 1948