perature dependence of i_C requires a knowledge of the temperature dependence of D_A, which unfortunately cannot be directly determined for tungsten(VI) in 12 M perchloric acid. Therefore, the data of Onstott[8] for the diffusion current of tetrachloroplatinate(II) ion in 0.1 M potassium chloride were used. A plot of log i/I, given in the last column of Table III, versus the reciprocal of absolute temperature, turned out to be linear. From the slope of the line, an activation energy of 13.4 kcal. per mole is calculated.

URBANA, ILLINOIS

Polarography of Tungsten(VI) in Hydrochloric Acid. Mechanism of the Tungsten(V)-Tungsten(III) Wave

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The reduction wave of tungsten(V) to tungsten(III) in hydrochloric acid or mixtures of hydrochloric acid and lithium chloride is shown to be unsymmetrical in shape. The plot of log $(i_d - i)/i$ versus potential shows two linear regions intersecting usually near the half-wave point. By applying the steady state treatment of Evans and Hush to the electrode process, and assuming that tungsten(V) is reduced directly to tungsten(III) but tungsten(III) returns via tungsten(IV) to tungsten(V) it is possible to account for the unsymmetrical wave form. From the observed slopes of the linear regions of the logarithmic plots, reasonable values of transfer coefficients are calculated.

Souchay[2] has studied the polarography of tungsten(VI) in weakly acidic solutions and in the heteropoly acids and Stackelberg, et al.,[3] reported a single reduction wave of tungsten(VI) in concentrated hydrochloric acid. The first thorough polarographic study of the various oxidation states obtainable in hydrochloric acid was made by Lingane and Small.[4] For tungsten(VI) they found two polarographic waves, the first of which began at a potential more positive than that of the oxidation of mercury, and corresponded to a reduction to tungsten(V). The second wave corresponded to the further reduction to tungsten(III) and was identical with the wave of tungsten(V) being reduced to tungsten(III).

It was remarkable, however, that although the reduction of tungsten(V) to tungsten(III) gave a wave of "reversible slope," the anodic curve of red tungsten(III) corresponded only to oxidation to tungsten(IV). Collenberg and Backer,[5] who studied the electrolytic reduction of alkali metal tungstates in concentrated hydrochloric acid, observed that as soon as the tungsten(V) state was passed, tungsten(IV) and tungsten(III) were produced simultaneously. At temperatures of 0 to 9°, appreciable quantities of tungsten(IV) were formed; at a temperature of 16–18°, red $Rb_2WCl_5 \cdot H_2O$ was formed and could be isolated, and at higher temperatures, the red tungsten(III) compound was transformed to the yellow-green $Rb_3W_2Cl_9$.

Lingane and Small[4] also observed the transformation of the red form to the yellow-green form, and presented evidence for a third intermediate colorless form of tungsten(III). From measurements of the cathode potential with interrupted current in coulometric reduction of tungsten(V)

and from observations of the color of intermediate solutions, it was concluded that "either tungsten(IV) or a compound of tungsten(V) and tungsten(III) is produced transiently" especially at higher initial concentrations of tungsten(V).

Collenberg and Backer[5] also electrolyzed 12-tungstosilicic acid and found that trivalent tungsten is formed before reduction to the +4 state was complete. They concluded that either the reductions W(V) → W(IV) and W(V) → W(III) occur simultaneously or that an effective +4 oxidation state is reached by reaction between tungsten(V) and tungsten(III).

In the present investigation, the shape of the rising portion of the tungsten(V) → tungsten(III) wave is interpreted by means of a kinetic treatment, in which the role of tungsten(IV) is clearly indicated.

Experimental

Preliminary experiments confirmed the observation by Lingane and Small[4] that the reduction wave of tungsten(V) is identical with the second wave of tungsten(VI). Therefore, for convenience, the same tungsten(VI) stock solution as previously described[6] was investigated in various media.

A Sargent Model III Manual Polarograph was used. Its "current multiplier," or sensitivity selector, had been calibrated potentiometrically against the voltage drop across a standard resistor. The potential setting was checked at every third or fourth reading against a Leeds and Northrup Student potentiometer. Corrections were made for iR drop by measuring the a.c. resistance in the conventional manner. The cell resistance was found to be quite appreciable, and to increase with increasing hydrochloric acid concentration (resistance values of 1730, 2180 and 2540 ohms, respectively, were observed for 8, 10 and 12 M hydrochloric acid in the conventional H-cell).

The rate of flow of mercury was determined by the procedure of Lingane and Kolthoff.[7] Values of m and t were determined in each of the media used and at each voltage at which diffusion currents were measured. The values of $m^{2/3}t^{1/6}$ were 1.680 ± 0.001 mg.$^{2/3}$sec.$^{-1/2}$ at −0.4 v. (vs. S.C.E.) and 1.697 ± 0.002 at potentials of −0.69 to −0.74 v., where the first and second wave heights were measured and did not vary appreciably with hydrochloric acid concentration. The mercury column height was 60.0 cm. and the temperature was 25.0 ± 0.1° in all experiments.

(1) Experimental work from Ph.D. Thesis of W. A. Ziegler, 1952.

(2) (a) P. Souchay, Ann. chim., **18**, 61, 73, 169 (1943); **19**, 102 (1944); **20**, 73, 96 (1945); (b) A. Tchakirian and P. Souchay, Ann. Chim., **1**, 232 (1946); (c) P. Souchay, Proceedings of the I. International Polarographic Congress, Prague, 1951, p. 327.

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

(4) J. J. Lingane and L. A. Small, THIS JOURNAL, **71**, 973 (1949).

(5) O. Collenberg and J. Backer, Z. Elektrochem., **30**, 230 (1924).

(6) H. A. Laitinen and W. A. Ziegler, THIS JOURNAL, **75**, 3045 (1953).

(7) J. J. Lingane and I. M. Kolthoff, ibid., **61**, 825 (1939).

Results

The polarographic data for the tungsten(V) → tungsten(III) step in various concentrations of hydrochloric acid are summarized in Table I. The data are essentially in agreement with those of Lingane and Small.

TABLE I
SECOND WAVE OF TUNGSTEN(VI) IN HYDROCHLORIC ACID

C_{HCl}, M	$C_{tungsten}$, mM	$-E_{1/2}$ (vs. S.C.E.)	i_d (cor.)	$i_d/Cm^{2/3}t^{1/6}$	Reciprocal slope Lower	Upper
12	0.575	0.543	2.30	2.34	0.038	0.063
12	1.150	.545	4.83	2.47	.034	.063
12	2.299	.529	9.61	2.44	.035	.058
10	0.575	.579	2.48	2.53	.032	.058
10	1.150	.574	4.90	2.50	.031	.057
8	0.575	.612	2.64	2.69	...	.051
8	1.150	.613	5.28	2.69	..	.051

However, the shape of the wave was not symmetrical, particularly in 12 M hydrochloric acid as is evident from the polarograms (Fig. 1) and especially the plot of log $(i_d - i)/i$ vs. E (Fig. 2). This plot can best be represented by two straight lines intersecting about at the half-wave point.

In 10 M hydrochloric acid, the log plot could be represented by two lines intersecting not at the half-wave point but about 20 mv. earlier.

In 8 M hydrochloric acid, the log plot was linear, with a reciprocal slope of 0.051, as though the steep portion had completely given way to the more shallow one.

A series of experiments was run in mixtures of hydrochloric acid and lithium chloride of total molarity equal to twelve. The essential data for the tungsten(V) to tungsten(III) wave are listed in Table II. Once again, the logarithmic plots could but be represented by two straight lines intersecting near the half-wave point. There seemed to be a slight trend of half-wave potential toward more positive potential with decreasing molarity of hydrochloric acid, but probably not enough to be significant.

TABLE II
SECOND WAVE OF TUNGSTEN(VI) IN HCl-LiCl MIXTURES

C_{HCl}, M	C_{LiCl}, M	$C_{tungsten}$, mM	$-E_{1/2}$ (vs. S.C.E.)	$i_d/Cm^{2/3}t^{1/6}$	Reciprocal slope Lower	Upper
10	2	0.575	0.542	2.27	0.040	0.078
10	2	1.150	.541	2.19	.040	.071
8	4	0.575	.534	2.03	.032	.076
8	4	1.150	.549	2.01	.031	.065
5	7	0.575	.513	1.67	.033	.048
5	7	1.150	.523	1.66	.035	.043

Another series was run in mixtures of hydrochloric and perchloric acids of total molarity equal to twelve. However, in this series a catalytic wave due to reduction of perchloric acid by tungsten(V) was encountered,[6] and no analysis of the shapes of the waves was possible.

Discussion

If we let (V), (IV) and (III) represent concentrations of the corresponding oxidation states of tungsten, and (V_0), (IV_0) and (III_0) the concentrations at the electrode surface, we may consider the six possible electron transfer reactions together
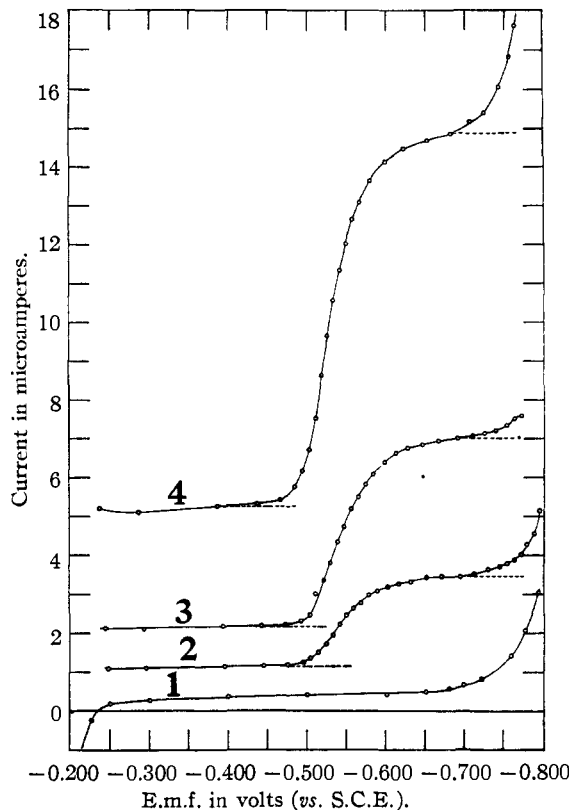

Fig. 1.—Polarograms of W(VI) in 12 M HCl: 1, residual current; 2, 0.575 mM W(VI); 3, 1.150 mM W(VI); 4, 2.299 mM W(VI).
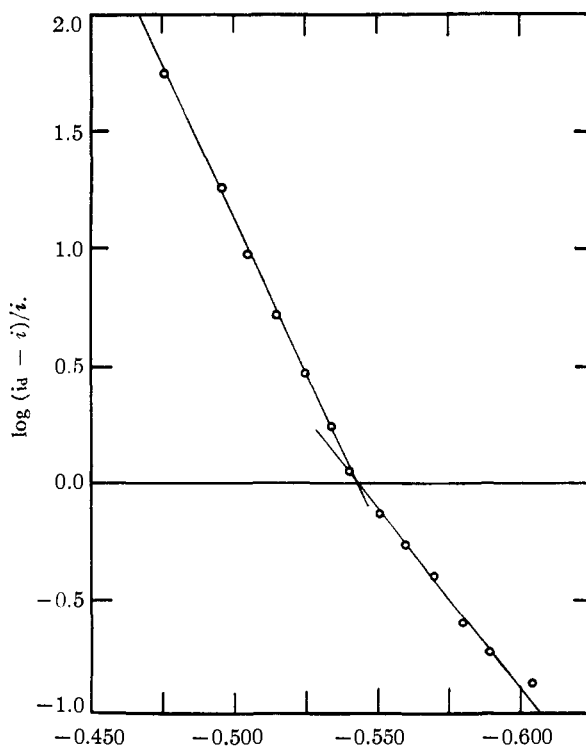

Fig. 2.—Log plot for W(V) → W(III) in polarogram of 0.575 mM W(VI) in 12 M HCl.

with the diffusion of V to the electrode and of III away from the electrode as a single reaction scheme,

following the steady state treatment of Evans and Hush[8] and Oldham.[9]

For the reduction of tungsten(V) to tungsten-(III) we have

$$V \underset{k_{dV}}{\overset{k_{dV}}{\rightleftarrows}} V_0 \quad \overset{k_5}{\underset{2e^-}{\longrightarrow}} \quad III_0 \quad \overset{k_{dIII}}{\longrightarrow} \quad III$$

In this scheme, k_1 to k_6 represent velocity constants (expressed in the two dimensional units cm. sec.$^{-1}$) for the corresponding electron transfer reactions and k_{dIII} and k_{dV} are diffusion rate constants in the same units. If, as in the present investigation, tungsten(VI) rather than tungsten(V) is present in the bulk of the solution, k_{dV} would be replaced by k_{dVI}, but the treatment would otherwise be the same.

The rate constants k_1, k_3 and k_5 for the forward electron transfer reactions may be related to potential by equations of the type

$$k_X = k_X^0 \exp \frac{-n_X \alpha_X EF}{RT} \tag{1}$$

α_1, α_3 and α_5 are the transfer coefficients for the reduction processes denoted by k_1, k_3 and k_5, and take constant values between zero and unity. For the oxidation reactions, the rate constants k_2, k_4 and k_6 are given by

$$k_y = k_y^0 \exp \frac{n_y \alpha_y EF}{RT} \tag{2}$$

where the sum of α_x and the corresponding α_y is unity.

The constants k_X^0 and k_y^0 are the values acquired by k_X amd k_y at the zero of the potential scale on which E is measured.

The diffusion rate constants k_{dIII} and k_{dV} may be related to diffusion coefficients by the equation

$$k_{di} = 1.231 \sqrt{D_i/t} \tag{3}$$

where t is the drop time, and 1.231 is a combination of pure numerical constants.

The steady state treatment regards the processes occurring at the electrode as obeying purely kinetic laws, and postulates that the concentrations (V_0), (IV_0) and (III_0) at the electrode surface are invariant with time, at a given potential. Thus, for example

$$k_{dV}(V) + k_2(IV_0) + k_6(III_0) - (k_{dV} + k_1 + k_5)(V_0) = 0 \tag{4}$$

Application of the treatment to the above scheme gives the relationship

$$\frac{i_d - i}{i} = \frac{k_{dV}}{k_{dIII}} \frac{k_2k_4 + k_2k_6 + k_3k_6 + k_2k_{dIII} + k_3k_{dIII}}{k_1k_3 + k_2k_5 + k_3k_5} \tag{5}$$

at any potential, E. The diffusion current, i_d, is given by

$$i_d = 2\bar{A}Fk_{dV}C \tag{6}$$

(8) M. G. Evans and N. S. Hush, J. chim. phys., 42, 159 (1952).
(9) K. B. Oldham, Ph.D. Thesis, University of Manchester, 1952.

where $\bar{A}$ is the mean electrode area, and C is the bulk concentration of V. This relationship is equivalent to the Ilkovic equation.

Since the polarographic and preparative electrochemical evidence cited above indicates that the reduction of tungsten(V) yields tungsten(III) directly whereas oxidation of tungsten(III) gives tungsten(IV) as the primary product, it is reasonable to assume that the rate constants k_4 and k_5 are large compared with k_3 and k_6. Introduction of this condition into equation (4) yields the expression

$$\frac{i_d - i}{i} = \frac{k_{dV}}{k_{dIII}} \times \frac{k_4 + k_{dIII}}{k_5} \tag{7}$$

Now k_{dIII} is independent of potential whereas k_4 decreases exponentially with increasing negative potential. Hence at the more positive potentials (foot of the reduction wave) $k_4 \gg k_{dIII}$, and therefore

$$\left(\frac{i_d - i}{i}\right)_{i \to 0} = \frac{k_{dV}}{k_{dIII}} \times \frac{k_4}{k_5} \tag{8}$$

whence

$$\left(\ln \frac{i_d - i}{i}\right)_{i \to 0} = \ln \frac{k_{dV}}{k_{dIII}} \times \frac{k_4^0}{k_5^0} + \frac{FE}{RT}[(1 - \alpha_3 + 2\alpha_5] \tag{9}$$

and

$$\left(\frac{d}{dE} \log \frac{i_d - i}{i}\right)_{i \to 0} = \frac{1 + 2\alpha_5 - \alpha_3}{0.0591} \text{ volt}^{-1} \text{ at } 25° \tag{10}$$

Conversely at the more negative potentials, $k_4 \ll k_{dIII}$, and similar reasoning gives

$$\left(\frac{d}{dE} \log \frac{i_d - i}{i}\right)_{i \to i_d} = \frac{2\alpha_5}{0.0591} \text{ volt}^{-1} \text{ at } 25° \tag{11}$$

Assuming that α_3 and α_5 are independent of potential and of the concentrations of tungsten(V), hydrogen ion and chloride ion, the above treatment predicts that in all the experiments described above a plot of log $(i_d - i)/i$ versus E should display two linear portions connected by a region of curvature (in which k_4 and k_{dIII} are comparable). Moreover the slopes of these linear portions should be independent of concentration as given by equations (10) and (11).

The results listed in Tables I and II indicate that the slope of the linear portions are subject to some variation, but show no definite trend with concentration.

Application of (10) and (11) to the values listed in Tables I and II gives

$$1 + 2\alpha_5 - \alpha_3 = 1.72 \pm 0.13$$
$$2\alpha_5 = 1.01 \pm 0.13$$

from which α_3 and α_5 are seen to be approximately 0.3 and 0.5, respectively. At large or small values of the ratio $(i_d - i)/i$, where the two linear portions occur, the slopes are very susceptible to small experimental errors and therefore it is possible to conclude only that the theoretical treatment leads to reasonable values for the calculated transfer coefficients, within the limits of experimental error in the current–voltage data.