

**745.** *Oxide Film Formation on the Surface of Metals in Aqueous Solutions and the Evaluation of their Standard Potentials. Part VI.\* The Tungsten Electrode.*

By (the late) S. E. S. EL WAKKAD, T. M. SALEM, H. A. RIZK, and J. G. EBAID.

Apparatus and technique are described for measuring the potential of a tungsten electrode in solutions of varying pH and initially free from tungsten ions. The true standard electrode potential, thus evaluated, is  $-1.0069$  v at  $25^{\circ}$ .

THE electrochemical behaviour of the tungsten electrode, in solutions of different pH values, is known<sup>1</sup> to depend upon whether it is in the massive or powdered form. The pH range has been determined over which it functions as an indicator electrode for hydrogen-ion activity. Electrodes which show potentials varying linearly with the pH of the solution are usually considered to contain an oxide film on the surface of the metal,<sup>2</sup> and this has been confirmed for the tungsten-tungsten trioxide electrode, the tungsten-blue electrode, and the anodic oxidation of tungsten at very low current density.

In this present investigation a technique has been developed for removal of the oxide film from tungsten and its true thermodynamic standard electrode potential has been determined.

#### EXPERIMENTAL

*Electrodes.*—Tungsten rod was cleaned with concentrated sodium hydroxide solution, rubbed with very fine emery paper till its surface was bright, washed with previously boiled and cooled conductivity water, and dried with filter paper.

*Solutions.*—These were as in Part V of this series.<sup>3</sup>

*Preparation of Electrodes and Solutions for Measurements out of Contact with Air.*—(a) *Chemical reduction with hydrogen at a high temperature.* The apparatus (Fig. 1) consisted of the tungsten rod electrode of diameter 0.4 cm. and length 5.5 cm., ground at one end for a distance of 1.5 cm. so that it fitted tightly in the ground end *P* of a silica tube when the apparatus was tilted vertically. The silica tube, 28 cm. long, was fitted by ground joints to two soda-glass tubes *A* and *B*. The joint *A* formed part of a small jacket, at the bottom of which a platinum wire spiral *R* was sealed to provide a connection between the electrode and the outer circuit, the connection being completed by mercury in the side tube, into which a bright copper wire electrode dipped. The spiral *R* was made in such a way that when the device was moved to the vertical position, the rod fitting tightly in *P*, also fitted conveniently into *R*. The silica tube was placed in an electric oven, then fitted with the jackets *A* and *B* with high-temperature grease and heated to remove the volatile components. The apparatus was then sealed at *D* to a high-vacuum pump and drawn out there to form a capillary constriction. The joint *B* was connected to another joint *O* ending in a sealed capillary tube *C*. When a high vacuum was attained pure hydrogen was introduced into the system. This evacuation and filling with hydrogen were repeated 3 times before the electrode was heated. Pure hydrogen introduced the third time was at a pressure of 1.2 atm. and the rod was then heated for 1 hr. at about  $950^{\circ}$ . Heating was then stopped and evacuation was carried out while the electrode was gradually cooling. When a high vacuum was attained and the temperature of the electrode reached room temperature the apparatus was sealed at *D* and tilted vertically, then fitted tightly into an electrode vessel similar to that used for mercury.<sup>2b</sup> The capillary tube *C* was broken, and the solution present in the electrode vessel thus admitted to the electrode jacket.

\* Part V, preceding paper.

<sup>1</sup> El Wakkad, Rizk, and Ebaid, *J. Phys. Chem.*, 1955, **59**, 1004; El Wakkad and Rizk, *ibid.*, 1957, **61**, 494.

<sup>2</sup> (a) Tourky and El Wakkad, *J.*, 1948, 740; (b) El Wakkad and Salem, *J. Phys. Colloid Chem.*, 1950, **54**, 1371; (c) Electrochem. Soc. Meeting, Cincinnati, Ohio, 1955, p. 60; El Wakkad, Salem, and El Chandour, *J. Egyptian Acad.*, 1956, No. 12, 7.

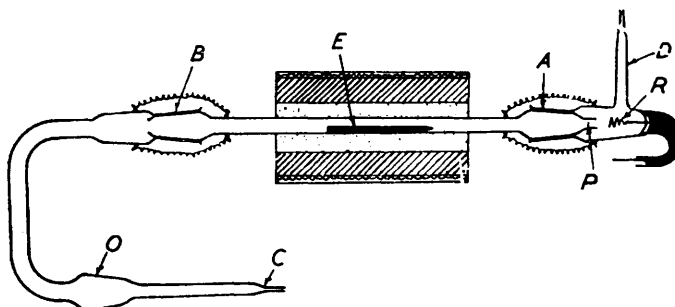
<sup>3</sup> Preceding paper.

(b) *Electrolytic reduction.* This method was based upon cathodic reduction of tungsten in strong alkali hydroxide solution, without exposure of the electrode to oxygen. The cathode was a tungsten rod 3 cm. long and 0.3 cm. thick and the anode was a platinum spiral 5 cm. long and 0.1 thick. Each electrode was sealed in a Pyrex glass tube, ground on the outside so that it fitted into an apparatus similar to that used for mercury<sup>4</sup> and tin. Reduction was carried out in pure nitrogen, which bubbled through the anode compartment to remove the oxygen evolved and prevent it from diffusion into the cathode compartment.

Solutions used for the determinations were freed as far as possible from dissolved oxygen by bubbling pure nitrogen into them. The hydrogen and nitrogen supplied from cylinders were purified as recommended by Noyes<sup>5</sup> and by Harcourt and Lupton<sup>6</sup> respectively. Measurements were carried out in an air-thermostat at  $25^\circ \pm 0.02^\circ$ . The reference half-cell was a saturated calomel electrode (for solutions free from tungsten ions) or a hydrogen electrode (when determining the standard electrode potential).

*Sodium Hydroxide Solutions.*—"AnalaR" sodium hydroxide was dissolved in about its own weight of conductivity water, transferred to a Pyrex glass tube lined with paraffin wax,

FIG. 1. Apparatus for reduction of tungsten electrode by hydrogen at  $950^\circ$ .



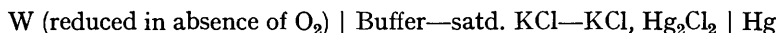
and left for several days to allow carbonate to settle. The clear supernatant solution was transferred in an atmosphere of pure nitrogen to the dilution apparatus described by Vogel.<sup>7</sup> Dilutions prepared from this solution were standardised against hydrochloric acid.

*Sodium Tungstate Solutions.*—From "AnalaR" anhydrous sodium tungstate solutions of known molarities were prepared by weight, and their strengths checked by means of the benzidine reagent.<sup>8</sup>

*Electrical Measurements.*—These were made in duplicate with independent stock solutions. The reference half-cell was the saturated calomel electrode whose potential with the liquid junction potential was 0.2448 v at  $25^\circ$ . E.m.f. measurements were carried out with a calibrated metre bridge similar to that used for mercury and tin.

## RESULTS AND DISCUSSION

Measurements were made in a cell of the type :



When the rod tungsten electrode was heated at  $950^\circ$  in hydrogen and then in a high vacuum, and then examined in oxygen-free buffer solutions the potential of the electrode was still a linear function of the pH of the solution. The  $E_{\text{H}^0}$  values was 0.15 (see from Fig. 2A), indicating that heating the tungsten electrode in hydrogen at  $950^\circ$  reduces the tungsten trioxide only to the intermediate product, tungsten blue.<sup>1</sup>

Fig. 2B shows that the potential of electrochemically reduced tungsten is constant from the extreme alkaline pH to about 11. Throughout this range the potential of the electrode in complete absence of oxygen is about  $-0.92$  v, the reproducibility within this

<sup>4</sup> El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621.

<sup>5</sup> Noyes, *J. Amer. Chem. Soc.*, 1907, **29**, 1718.

<sup>6</sup> Harcourt and Lupton, *J. Chem. News*, 1876, **33**, 90.

<sup>7</sup> Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1939, p. 286.

<sup>8</sup> *Idem*, *op. cit.*, 1948, p. 575.

range of pH being of the order of 12 mv. This value is not in agreement with the calculated values<sup>1</sup> of  $E_B^0$  of any of the oxides of tungsten ( $WO_2$ ,  $W_2O_5$ ,  $WO_3$ ). At such extreme ranges of pH one must also expect that oxides of tungsten possess higher solubilities, if ever formed on the surface of the electrode. In solutions with pH values lower than 11 the protected electrode began to show potentials which varied linearly with pH. However, the slope of curve B is greater than that expected for an electrode acting as a pH indicator. This is in accordance with findings by El Wakkad *et al.*<sup>1</sup> and Baylis.<sup>9</sup> Antimony electrodes, which act as hydrogen electrodes, behave similarly.<sup>10</sup> The  $E_H^0$  value was  $-0.05$  v, in good agreement with the value calculated from the reaction:  $W + 2H_2O = WO_2 + 4H^+ + 4e$ .

*Evaluation of the Standard Potential of Tungsten.*—For this determination the tungsten electrode was reduced cathodically in a strongly alkaline solution. The standard electrode potential of tungsten-tungstate ion was determined in alkaline hydroxide solutions where the tungsten electrode is not covered with an oxide film; further, in these strong solutions

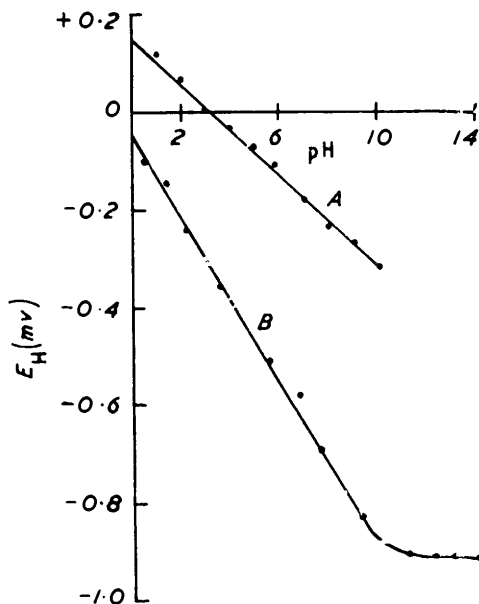
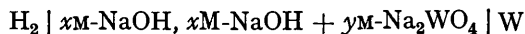
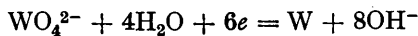


FIG. 2. Voltage-pH curves.  
A, Electrode heated in hydrogen.  
B, Electrode reduced electrochemically.

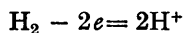
there will be no tendency for the formation of polytungstate.<sup>11</sup> There is no previous determination of such standard electrode potentials and only an approximate value based on thermal data was given by Latimer.<sup>12</sup> The cell was of the type:



$y$  being small compared with  $x$ , the two solutions became nearly identical and the liquid junction potential became negligible. Measurements were made out of contact with air. The reaction taking place in the tungsten half-cell can be represented as:



In the case of the hydrogen half-cell, the reaction taking place is:



<sup>9</sup> Baylis, *Ind. Eng. Chem.*, 1923, **15**, 852.

<sup>10</sup> El Wakkad, *J.*, 1950, 2894; Parks and Beard, *J. Amer. Chem. Soc.*, 1932, **54**, 856; Perley, *Ind. Eng. Chem. Anal.*, 1932, **54**, 856.

<sup>11</sup> El Wakkad and Rizk, *J. Phys. Chem.*, 1957, **61**, 494.

<sup>12</sup> Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938, p. 237.

Since tungsten and hydrogen are at their standard states, it is only necessary for calculating the standard electrode potential at  $W/WO_4^{2-}$  to determine the activity of the hydrogen ion in the hydrogen half-cell and that of the tungstate ion in the  $W/WO_4^{2-}$  half-cell. By following the procedure of Lewis and Randall<sup>13</sup> for calculating the activity coefficient at

NaOH (M)	Na <sub>2</sub> WO <sub>4</sub> (M)	E.m.f. (v)	E <sub>0</sub> (v)	NaOH (M)	Na <sub>2</sub> WO <sub>4</sub> (M)	E.m.f. (v)	E <sub>0</sub> (v)
0.1	0.01	0.1672	-1.0086	0.025	0.00020	0.1592	-1.0075
0.1	0.005	0.1564	-1.0061	0.025	0.00010	0.1499	-1.0069
0.1	0.0025	0.1478	-1.0058	0.025	0.00005	0.1408	-1.0067
0.05	0.00125	0.1609	-1.0063				
0.05	0.00100	0.1595	-1.0078				
0.05	0.00050	0.1498	-1.0069				

various ionic strength, the standard electrode potential of  $W/WO_4^{2-}$  was calculated and is given in the Table: the mean value is  $-1.0069 \pm 0.0004$  v at 25°, as compared with value of -1.1 v obtained by Latimer<sup>12</sup> from thermal data.

The authors thank Dr. A. Hickling for reading the manuscript.

CAIRO UNIVERSITY, FACULTY OF SCIENCE, CAIRO.  
EIN SHAMS UNIVERSITY, UNIVERSITY COLLEGE FOR GIRLS, CAIRO, EGYPT.

[Received, January 17th, 1957.]

<sup>13</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York, 1923, p. 334.