in a comparison furnace *vs.* a Bureau of Standards thermocouple through the courtesy of Mr. H. A. Brown, of this company. The temperature of the bomb furnace was recorded by a Brown Instrument Co. thermocouple potentiometer. Reservoir A and the attached manometer were used for volume calibration of the system at various temperatures. Both hydrogen and argon were used as calibrating gases. Reservoir J was used to admit known volumes of purified hydrogen to the system at high pressures.

Materials.—"Water-pumped" electrolytic hydrogen from a single selected cylinder was purified by passage over incandescent zirconium in the high-pressure getter system G'G which quantitatively removed oxygen, moisture, nitrogen and carbonaceous impurities. Extreme precautions must be taken to purify even the best available hydrogen. Samples of titanium from both the Bureau of Mines and the du Pont Co. were used. The 99.02% metal was heated slowly to 350° in a vacuum furnace protected by titanium getters and allowed to degas. (Higher temperatures fix the adsorbed gases otherwise evolved.) When a vacuum of 0.1 micron was obtained, the temperature was raised very slowly to 1000° and held for 1.5 hr. Hydrogen purified by passage over (a) palladium catalyst, (b) Drierite, (c) a mixture of titanium sponge and zirconium powder at 850° was admitted and the temperature reduced over 9 hr. to 375°, then over 16 hr. to 25°. Considerable amounts of volatile metals including magnesium and silicon were lost during evacuation and the resulting hydride samples analyzed 94.4% Ti, 3.99-4.00% H, 0.01-0.03% N, 0.03-0.08% C, 0.01-0.08% Si, 0.1% Mg, and less than 0.1% Mn, Ca, Cu. In all cases spectrographic analysis showed other metallic impurities to be substantially absent. Chloride, sulfur, and oxygen were not determined. (The chemical analysis for Ti cited above was somewhat lower than that obtained by quantitative hydrogen absorption.) The brittle hydride was ground in an argon- or nitrogen-filled dry box and loaded into the previously treated bombs through the capillary stem. The bombs were degassed at 100° and flushed repeatedly with purified hydrogen before used. Analysis after several months of use showed no change beyond the limits of analytical error except for a pick-up of fractional percentages of chromium, manganese, and iron from the bombs. The argon and nitrogen gases used were of guaranteed purity 99.99%. The argon was found to be moist, however, and was dried by passage over Drierite.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

The Anodic Oxidation of Thallous Ion on the Rotating Platinum Microelectrode

BY PAUL DELAHAY AND G. L. STIEHL[1]

Thallous ion is irreversibly oxidized to thallic hydroxide on a rotating platinum microelectrode. The corresponding anodic wave can be observed above *p*H 7.85. At lower *p*H the evolution of oxygen interferes. The overvoltage decreases as the *p*H increases. Half-wave and decomposition potentials are compared with potentials calculated from thermodynamic data.

The anodic oxidation of thallous ion in acid solutions has been reported by Grube and Hermann[2] but this reaction has not been investigated in neutral or alkaline solution as far as we know. The application of the rotating microelectrode to the study of this reaction is reported in the present paper.

Experimental

Since the oxidation of thallous ion occurs at rather highly positive potentials, the dropping mercury electrode cannot be used. Good waves were obtained with the rotating microelectrode described by Laitinen and Kolthoff.[3] Waves were recorded with a "Sargent" manual polarograph model III. A polarographic cell with a mercury pool and the H-cell designed by Lingane and Laitinen[4] were used. Before determining a wave the microelectrode was cleaned in concentrated sulfuric acid to dissolve any thallic hydroxide which might have been deposited in a previous experiment. Distorted waves were observed when the microelectrode was not thoroughly cleaned. The values of the *p*H below 10 were measured with a Beckman model G instrument. Values above *p*H 10 were calculated. Dissolved oxygen did not interfere.

Description of Wave and Discussion of Results

Anodic waves obtained in various media from *p*H 7.85 to pH 13.7 are shown in Fig. 1. Waves are arbitrarily shifted along the vertical axis in this diagram. No distinct wave could be observed below *p*H 7.85 because of the simultaneous evolution of oxygen. Waves are shifted toward more positive potentials as the *p*H decreases. This can be expected from the dependence of the equilibrium potential on *p*H according to the formula

$$E = 1.19 - 0.0886pH - 0.0295 \log a_{Tl^+} \quad (1)$$

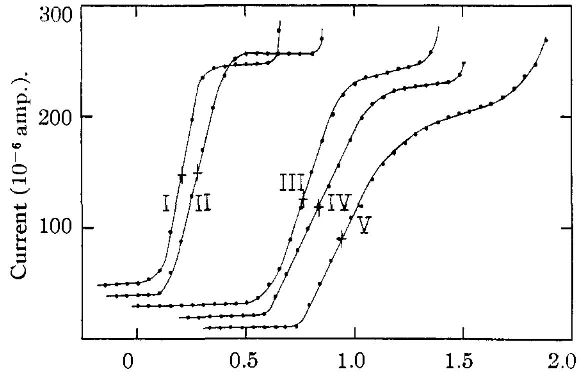

Fig. 1.—Anodic waves of 10^{-3} molar Tl^+ solutions at various *p*H: I, *p*H 13.7, NaOH 0.5 *N;* II, *p*H 13.0, NaOH 0.1 *N;* III, *p*H 11.0, NH_4OH and $(NH_4)_2SO_4$ buffer in KNO_3 0.1 *N;* IV, *p*H 9.20, borate buffer; V, *p*H 7.85 phosphate buffer.

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[1] This paper is part of a dissertation to be submitted to the Graduate School of Louisiana State University by G. L. Stiehl in partial fulfillment of the requirements for the degree of Master of Science.

[2] Grube and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Laitinen and Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

[4] Lingane and Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

The standard potential in formula (1) was calculated from thermodynamic data[5] by assuming that thallic hydroxide was the product of the anodic process according to the reaction

$$\mathrm{Tl^+ + 3H_2O = Tl(OH)_3 + 3H^+ + 2e^-} \qquad (2)$$

Thallic ion was not taken into consideration because of the low solubility of the hydroxide.

Equilibrium potentials given by equation (1) are plotted against *p*H in Fig. 2 for the activity $a_{\mathrm{Tl}^+} = 10^{-3}$. Experimental decomposition and half-wave potentials are plotted on the same diagram. It was observed that these experimental potentials fluctuated as different platinum microelectrodes were used. These fluctuations were probably caused by variations of the surface of the electrode. By comparing lines I and II with line III of Fig. 2 one concludes that reaction (2) is irreversible on a platinum microelectrode and that the overvoltage decreases as the *p*H increases.

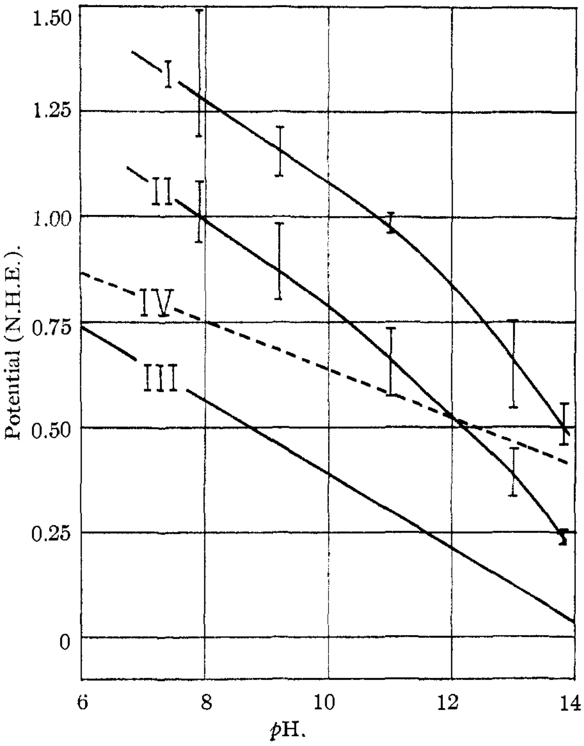

Fig. 2.—Decomposition and half-wave potentials as a function of *p*H for 10^{-3} molar $\mathrm{Tl^+}$ solutions: I, half-wave potential; II, decomposition potential; III, equilibrium potential; IV, equilibrium potential for the evolution of oxygen.

Reaction (2) takes place on a platinum electrode in a range of potentials where the oxidation of water to oxygen is possible. The equilibrium conditions for this latter reaction is represented in Fig. 2 by line IV. Actually, the oxidation of water to oxygen requires a large overvoltage and the anodic wave for thallous ion is observed at or above *p*H 7.85. In neutral or acid media both reactions occur in the same range of potentials and no distinct wave is observed.

The dependence of the wave height on the concentration of thallous ion was investigated. Sodium hydroxide 0.1 *N* or 0.5 *N* gave the best results. The data of Table I indicate that the proportionality relationship between wave height and concentration is verified in the 0.05 to 1 millimolar concentration range. The results are not reliable as indicated by the large error for the data obtained with the 0.2 and 0.5 millimolar solutions. The main source of error is probably the coating of the electrode by thallic hydroxide and the resulting variation in the working area of the electrode. This interpretation is substantiated by the fact that the diffusion current, measured at a constant potential corresponding to the upper plateau of the wave, decreases slowly in the course of time.

TABLE I

VARIATIONS OF WAVE HEIGHT WITH CONCENTRATION OF THALLOUS ION IN 0.1 *N* SODIUM HYDROXIDE

Concentration, millimole per liter	Wave height, microamperes
0.05	8.3
.1	17.6
.2	25.1
.5	72.5
1	171.5

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[5] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall Inc., New York, N.Y., 1938, p. 153.