

**744.** *Oxide Film Formation on the Surface of Metals in Aqueous Solutions and the Evaluation of their Standard Potentials. Part V.\* The Tin Electrode.*

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The behaviour of the electroplated tin and tin-amalgam electrodes in solutions of varying pH, initially free from tin ions, is examined from the extreme acid to the extreme alkaline range, and the probable existence of an oxide film on the surface of metals discussed. A new technique is described for measuring the potential of tin out of contact with air.

By comparing the results obtained in such solutions in and out of contact with air a set of conditions was chosen leading to the evaluation of the true standard electrode potential. That for tin was thus found to be  $-0.1375$  v at  $25^\circ$ , compared with the value of  $-0.1364$  v in air.

In our previous investigations<sup>1</sup> an oxide was found to exist on the surface of metals in aqueous solutions. The effect of this film on the thermodynamic potential of the electrode has been discussed and a new technique introduced for measuring the standard potential of these metals out of contact with atmospheric oxygen (*i.e.*, under conditions such that no film exists).

The present investigation deals with metallic tin, concerning which the limited work already reported<sup>2,3</sup> is conflicting. We have studied the growth of an oxide film on tin, and the behaviour of the electrode over a wide pH range in the presence and absence of air and after removal of the oxide film, and have thus determined the true standard electrode potential.

\* Part IV, *J. Egypt. Acad.*, 1956, No. 12, 7.

<sup>1</sup> Tourky and El Wakkad, *J.*, 1948, 740; El Wakkad and Salem, *J. Phys. Colloid Chem.*, 1950, **54**, 1371; Electrochem. Soc. Meeting, Cincinnati, Ohio, May, 1955, p. 60; El Wakkad, Salem, and El Ghandour, *J. Egyptian Acad.*, 1956, No. 12, 7, in the press.

<sup>2</sup> Hoar, *Trans. Faraday Soc.*, 1937, **33**, 1152; Haring and White, *Trans. Electrochem. Soc.*, 1938, **73**, 11.

<sup>3</sup> Noyes and Toabe, *J. Amer. Chem. Soc.*, 1917, **39**, 1537.

## EXPERIMENTAL

*Tin Electrodes.*—Tin electrodes were prepared by electrodeposition from a solution of stannous chloride dihydrate (2.8 g.) in 2*N*-sodium hydroxide (40 c.c.) at 2 mA/electrode for 10 min. at 80° on a platinum wire 1 cm. long and 0.1 cm. in diameter. The electrode was washed several times with conductivity water, then with the solution in which the measurements were carried out.

For preparation of tin-amalgam electrodes a similar platinum wire was electroplated with mercury at 3 mA/electrode for 30 min. from dilute nitric acid saturated with mercurous nitrate at 25°. The electrode was washed several times with conductivity water, then electroplated with tin as just described. A fresh plating was used for each experiment.

*Buffer Solutions.*—These covered the pH range 1.0—11.36, as follows: pH 1.0—2.2, solutions prepared from hydrochloric acid and potassium chloride;<sup>4</sup> pH 3.61—5.63, acetic acid—acetat;<sup>5</sup> pH 6.77—9.24, boric acid—borax;<sup>6</sup> pH 10.17—11.36, sodium carbonate—hydrochloric acid.<sup>7</sup> For the extreme acid and alkaline ranges hydrochloric acid and sodium

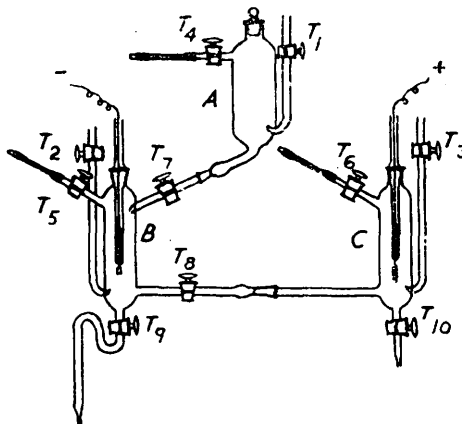


FIG. 1. Apparatus for measurements out of contact with air.

hydroxide solutions were used. All solutions were prepared from highly purified materials and their pH values checked with the hydrogen electrode and, when possible, with the quinhydrone electrode.

*Preparation of Electrodes and Solutions for Measurements out of Contact with Air.*—For this an electrochemical method was based upon our studies of the anodic behaviour of tin.<sup>8</sup> It consisted of cathodic reduction of tin or tin amalgam in the solution in which the measurements were carried out, all operations being carried out in an atmosphere of nitrogen (from cylinders and purified as recommended by Harcourt and Lupton<sup>9</sup>). The apparatus is shown in Fig. 1. The cell resembled that used for mercury.<sup>10</sup> Its three compartments *A*, *B*, and *C* were fitted to each other by very tight ground joints. Taps 1, 2, and 3 were for the inlet of nitrogen, and 4, 5, and 6 for outlet. Taps 7 and 8 served for transference of the solutions from one compartment to the other, and taps 9 and 10 for their discharge. The cathode present in compartment *B* was a platinum plate of surface area 1 sq. cm., electroplated with tin or tin amalgam as described above. The anode in compartment *C* was a platinum spiral 5 cm. long and 0.1 cm. thick. The solutions used were boiled and cooled in an atmosphere of pure nitrogen and introduced into compartment *A*, then were allowed to pass through *B* and *C*. The tin electrode was reduced cathodically with a polarising current of about 6 mA/electrode for about an hour, in an atmosphere of pure nitrogen which was allowed to bubble through the solution present even in the anode compartment *C* to remove the oxygen evolved and prevent its diffusion into

<sup>4</sup> Clark and Luba, cited in Britton's "Hydrogen Ions," Chapman and Hall, London, 1932, p. 301.

<sup>5</sup> Cohn, *J. Amer. Chem. Soc.*, 1927, **49**, 173.

<sup>6</sup> Palitzsch, cited in Britton's "Hydrogen Ions," see ref. 4, p. 219.

<sup>7</sup> Kolthoff, cited in Britton's "Hydrogen Ions," see ref. 4.

<sup>8</sup> El Wakkad, El Din, and El Sayed, *J.*, 1954, 3103.

<sup>9</sup> Harcourt and Lupton, *J. Chem. News*, 1876, **33**, 90.

<sup>10</sup> El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621.

the solution in the cathode compartment *B*. After complete cathodic reduction taps, 2, 5, 7, 8, and 9 were closed and the cathodic compartment *B* was released from the other two compartments to be connected through the tap 9 to the reference half-cell which was either the saturated calomel electrode (when examining the electrode behaviour in solutions free from tin ions) or a hydrogen electrode (when determining the standard electrode potential). The pH value of each solution used was checked directly before and after electrolysis and never varied by more than 0.08 pH unit after electrolysis.

*Stannous Perchlorate.*—This was prepared as recommended by Noyes and Toabe,<sup>3</sup> *i.e.*, indirectly. "AnalaR" cupric oxide was dissolved in an excess of boiling diluted "AnalaR" perchloric acid, individual dilutions being standardised against sodium carbonate. Then tin shavings were added in large excess. The copper separated completely as a spongy deposit, leaving a colourless solution of stannous perchlorate, which was filtered through asbestos in an atmosphere of carbon dioxide and in contact with metallic tin, and kept in glass-stoppered bottles filled with carbon dioxide and containing metallic tin. From this stock solution various dilutions were prepared and used within 12 days. During this period the conductance of the stock solution was determined every 2 days in an evacuated conductivity cell; the conductance remained constant, showing that the ion concentration did not change during this period in spite of the development of a yellow colour; the solution remained clear. The molarity of ten perchlorate in the stock solution was determined by titration under carbon dioxide against 0.1*N*-potassium permanganate, after further acidification with 20% perchloric acid. Free perchloric acid in the stock solution was determined by diluting a weighed portion and saturating it with hydrogen sulphide; after the tin sulphide has settled, it was filtered off and washed until free from acid, and the filtrate was boiled for 20 min. to remove hydrogen sulphide, cooled, and titrated with 0.1*N*-sodium hydroxide to phenolphthalein; subtracting from the acid thus found the number of equivalents of tin present gave the quantity of free acid in the solution. The stock solution was analysed for both perchlorate and free perchloric acid before every dilution. The results obtained were always in satisfactory agreement with each other.

The molarity of perchloric acid chosen varied between 0.05 and 0.005*M*, while those of stannous perchlorate were from 0.016999 to 0.000212*M*. However, this variation lies within the range of pH in which the potential measurements with a tin electrode are not contaminated by oxide formation.

*Electrical Measurements.*—The measurements were carried out in duplicate with different stock solutions. In the buffer solutions the measurements were performed with a saturated calomel electrode as the reference half-cell. The procedure suggested by Harned and Owen<sup>11</sup> was used, and the experimental  $E_0$  pH value of our saturated calomel electrode, determined in buffers with acids of known dissociation constants and after the necessary corrections, was taken as 0.245 v at 25°. The cells were kept in an air-thermostat at 25° ± 0.02°.

The e.m.f. measurements were carried out with a calibrated metre bridge on which accurate readings could be taken to 0.02 cm. A cadmium cell calibrated by the National Physical Laboratory and an Onwood mirror galvanometer having a sensitivity of 190 mm./10<sup>-6</sup>A were used.

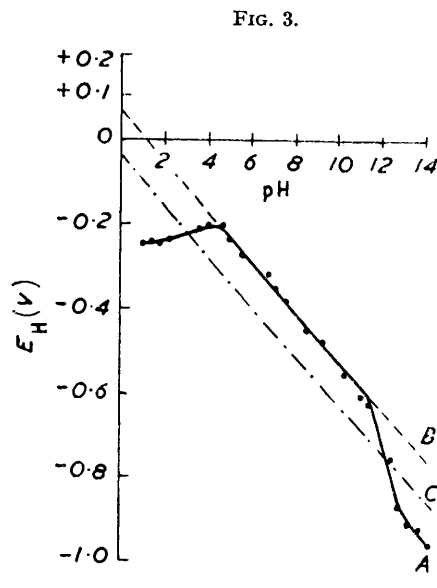
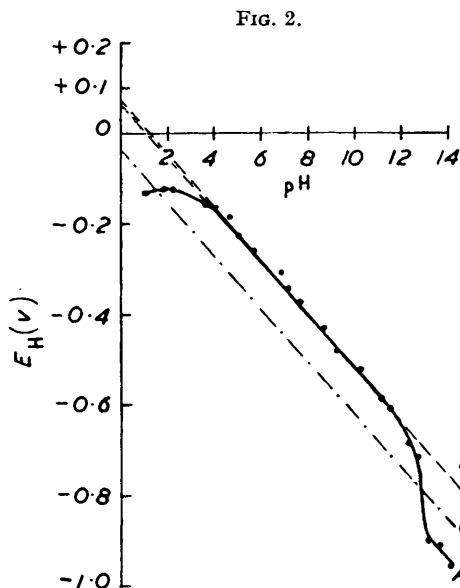
## RESULTS AND DISCUSSION

*Behaviour of the Electrode in Solutions of Various pH, initially containing no Tin ions, in Air.*—The potential-pH curves (Figs. 2*A* and 3*A*) for the electroplated tin electrodes and tin-amalgam electrodes respectively in unstirred solutions of varying pH, show that the potential of both types of electrodes varies linearly with the logarithm of the hydrogen-ion activity of the solution from pH 5 to 11 for the former electrode and from pH 3.6 to 11 for the latter. For the extreme acid region and the extreme alkaline region the potential values of such electrodes deviate, however, from the theoretical for the hydrogen electrode. The values obtained in the acid region for the tin-amalgam electrode are more positive than those of the electroplated tin electrode. From pH 11 to 12.6 both electrodes show irregular variation in potential. The  $E_H^0$  values for the tin and the amalgamated-tin electrode are 0.065 and 0.075 v respectively. Curves *B* in Figs. 2 and 3 show the theoretical curve for Sn(OH)<sub>2</sub>/Sn(OH)<sub>4</sub> while curves *C* in the same figures are for Sn/Sn(OH)<sub>2</sub>.

<sup>11</sup> Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 311.

The behaviour of metals which show a potential varying linearly with pH is usually attributed to the formation of an oxide film on the surface of the metal (El Wakkad *et al.*<sup>11</sup>), and thus the electrode behaves as a metal-metal oxide electrode.

To ascertain which type of oxide is formed one must calculate from the thermal data the potentials of the different oxides of tin to see which of them agrees with the experimental results. If the free energy of  $\text{Sn(OH)}_2$  is taken as  $-115,200$  cal. and that of  $\text{OH}^-$  as  $-37,585$  cal.,<sup>12</sup> the free energy change of the reaction,  $\text{Sn} + 2\text{OH}^- = \text{Sn(OH)}_2 + 2e$ , is  $\Delta F = -40,030$  cal. This gives an  $E_B^0$  value (potential values at the extreme alkaline range of pH) of  $-0.87$  v at  $25^\circ$ . Applying the ordinary equation for the variation of the potential of a metal-metal oxide electrode with the pH, we obtain  $E_H^0$  for the  $\text{Sn-Sn(OH)}_2$



Figs. 2 and 3. Potential-pH curves for (Fig. 2) tin-amalgam and (Fig. 3) tin electrodes, in presence of air.

A, Experimental values. B, Theoretical values for  $\text{Sn(OH)}_2/\text{Sn(OH)}_4$ . C, Theoretical values for  $\text{Sn}/\text{Sn(OH)}_2$ .

electrode a value of  $-0.05$  v. Taking the free energy of formation of stannic hydroxide as  $-226,000$  cal. gives the free-energy change of the reaction,  $\text{Sn(OH)}_2 + 2\text{OH}^- = \text{Sn(OH)}_4 + 2e$ , as  $-35,630$  cal. and thence  $E_B^0 = -0.77$  v, so that  $E_H^0$  is  $+0.05$  v.

This indicates that  $\text{Sn(OH)}_4$  is formed on the surface of metallic tin in aqueous solutions in air and that this oxide is responsible for the linearity in the potential pH curve.

For the region in the potential-pH curve from pH 11 to 12.6, the irregularity can be attributed to the probable amphoteric character of stannic hydroxide. However, this break corresponds actually to the region of the isoelectric point of such a hydroxide,<sup>13</sup> and analogous findings have been made before in this laboratory.

In the acid range the lack of linearity for both electrodes can be attributed to the primary formation, on the surface, of stannous hydroxide which tends to saturate the double layer; owing to the great solubility of the oxide in such solutions, this will lead

<sup>12</sup> Latimer, "The Oxidation States of Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938, p. 199.

<sup>13</sup> Dey and Ghosh, *Proc. Nat. Inst. Sci. India*, 1946, **15**, A, 143.

to variation in the pH of the solution at the interphase, causing it to increase so that the potential will be lower than expected. The local change of pH in the vicinity of the electrode was found previously for mercury<sup>14</sup> and tungsten.<sup>15</sup> This is confirmed for the present case when the results obtained with tin and tin-amalgam electrodes are compared: the latter, being more protected, give more positive potential values.

From pH 12.6 to the extreme alkaline range the potential value deviates from the theoretical one for the hydrogen electrode. It is suggested that in this region stannous hydroxide, when first formed on the surface of the electrode, dissolves freely giving stannite which is unstable and decomposes to stannate. The free-energy change of the reaction,  $\text{Sn} + 6\text{OH}^- = \text{Sn}(\text{OH})_6^{2-} + 2e$ , is  $\Delta F = -80,490$  cal. and so  $E_B^0$  is  $-1.74$  v, which is a very negative potential value when compared with the potential obtained,  $-0.96$  v. This suggests that, in alkaline solutions, owing to dissolution of stannous oxide, the hydroxyl-ion concentration decreases in the vicinity of the electrode, and hence the potential value measured becomes more positive than expected.

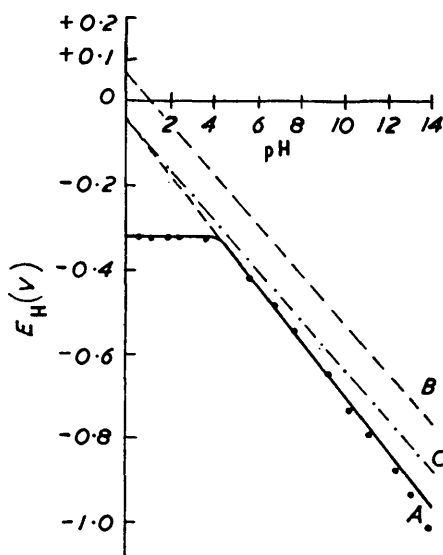


FIG. 4. Potential-pH curves for tin or tin-amalgam electrodes, in absence of air. A, B, C, As for Figs. 2 and 3.

*Behaviour of the Electrode in Solutions of Various pH, initially containing no Tin Ions, out of Contact with Air.*—To remove the oxide from the surface of the electrode and eliminate the effect of atmospheric oxygen, the tin electrode was reduced electrolytically as described above. Fig. 4 shows the variation of the potential of both the electrochemically reduced tin and the tin-amalgam electrode with the pH of the solution. In solutions having  $\text{pH} > 4.5$ , these potentials are a linear function of the pH. The  $E_H^0$  value for this portion of the curve was  $-0.040$  v. The linearity was due to the formation of stannous oxide, and this value found is in good agreement with the theoretical value previously calculated. At the extreme alkaline region ( $\text{pH} 13$  and  $14$ ) the negative potential values obtained are due to the formation of stannate. The formation of an oxide film on the surface of metals out of contact of air, in comparatively alkaline solutions, can be attributed to the increase of hydroxyl-ion concentration: a state is expected to be reached where hydroxyl ion together with the metal ions present will saturate the interphase with the metal hydroxide so that the metal starts to function as a metal-metal oxide electrode.

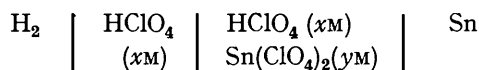
From pH 1 to 4.5 the potential constant for both electrodes is about  $-0.320$  v. When

<sup>14</sup> El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621.

<sup>15</sup> El Wakkad, Rizk, and Ebaeid, *ibid.*, 1955, **59**, 1004.

a pure metal is dipped in an aqueous solution containing no ions of this metal, and in absence of dissolved oxygen which may act as electron acceptor, the potential of this metal in the comparatively acid solution is expected to be extremely negative, leading to dissolution of the metal and discharge of hydrogen ions. The potential observed in this case is expected to be governed by the potential of the hydrogen electrode at the corresponding pressure and the pH prevailing within the double layer, and also by the hydrogen overpotential on the particular metal. This indicates the absence of any oxide film from the surface of the metal from the extreme acid range of pH to about pH 5 in solutions freed from dissolved oxygen. The evaluation of the standard electrode potential of tin under these conditions in solutions of pH values less than 5 will therefore give the exact thermodynamic reversible value.

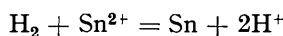
*Evaluation of the Standard Potential of Tin.*—The cell used was of the type :



$y$  was made small compared with  $x$ , so that the two solutions became nearly identical and the liquid junction potential became negligible.

Measurements were made out of contact with air, and for comparison the same cell was studied without this extreme protection.

The reaction taking place in the tin half-cell can be expressed as :



Thus

$$E = E_0 - \frac{RT}{2F} \log \frac{a_{\text{Sn}} a_{\text{H}^+}^2}{a_{\text{H}_2} a_{\text{Sn}^{2+}}}$$

Since tin and hydrogen are at their standard states this equation at 25° reduces to :

$$E = E_0 - \frac{0.0591}{2} \log \frac{a_{\text{H}^+}^2}{a_{\text{Sn}^{2+}}}$$

For calculation of the standard electrode potential, it is only necessary to determine the activity of  $\text{H}^+$  in the hydrogen half-cell and that of  $\text{Sn}^{2+}$  in the tin-stannous perchlorate half-cell. Following the procedure of Lewis and Randall<sup>16</sup> for calculating the activity coefficient of various ionic strengths gives the  $E_0$  values for unprotected and protected electrodes shown in the Table. The  $E_0$  value obtained in air is  $-0.1364$  v, and that out of contact with air is  $-0.1375$  v, which is the true standard electrode potential of tin. The maximum error in our measurements is  $\pm 0.0005$  v.

$\text{HClO}_4$ (M)	$\text{Sn}(\text{ClO}_4)_2$ (M)	$E_0$ (in air) (v)	$E_0$ (v)	$\text{HClO}_4$ (M)	$\text{Sn}(\text{ClO}_4)_2$ (M)	$E_0$ (in air) (v)	$E_0$ (v)
0.05	0.016999	-0.1363	-0.1373	0.005	0.000849	-0.1367	-0.1378
0.05	0.008499	-0.1370	-0.1370	0.005	0.000424	-0.1368	-0.1374
0.05	0.004249	-0.1369	-0.1370	0.005	0.000212	-0.1362	-0.1376
0.01	0.003399	-0.1361	-0.1378				
0.01	0.001699	-0.1360	-0.1377				
0.01	0.000849	-0.1362	-0.1375				

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<sup>16</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York, 1923, p. 334.