148. *Studies on Some Metal Electrodes. Part III. Does the Antimony Electrode behave Simply as a Metal–Metal Oxide Electrode in Air?*

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Consideration of the values assigned by different authors to the term E_0' of the antimony electrode reveals that values approaching the thermodynamic one of 0·140 v. are only obtained when the finely divided metal is involved in the electrode system; otherwise, values more positive by ~100 mv. are obtained. This is explained by postulating that the behaviour of the electrode in air is governed by an oxygen overvoltage effect due to the persistence on its surface of oxygen doublets. The overvoltage effect is in harmony with the results of previous investigations on thin films on metal surfaces as affecting their electrochemical behaviour, and explains satisfactorily the behaviour of massive and electrodeposited electrodes at the steady states in air. It is suggested that as such the antimony electrode should be distinguished as a metal–metal oxide–oxygen electrode.

Examination of the vast amount of literature on the antimony electrode reveals that, although most authors agree that it can function satisfactorily as an indicator electrode in acid–base titrations, yet it cannot serve for the accurate determination of pH unless it is previously calibrated. This is generally based on the fact that the electrode does not always follow a theoretical relation, as should be the case if it functioned properly as a metal–metal oxide clectrode. The disparity in the values pertains not only to the term E_0' or to $\Delta E/\Delta\text{pH}$, but also to the range of pH within which the electrode functions as an indicator electrode.

In this and the following paper the attempt is made to clarify the situation by comparing the behaviour of that electrode in and out of contact with air, taking into account the amphoteric and other properties of the oxide(s) formed on the metal. Studies upon these lines have not been made before, but, as will be seen, they lead to a fruitful theory with the help of which the mechanism of this and other similar electrodes may be explained.

Experimental.

Electrodes.—The electrodes used were of two types: a stick antimony electrode, and electrodes prepared by deposition on bare platinum, the deposition being made immediately before each measurement. We shall designate the two types by the letters A and B, respectively. Electrode A consisted of a rod of pure antimony (from Hellige, in Freiburg) 3 cm. long and 0·7 cm. in diameter, fitted tightly at one end of a glass tube that could be filled with mercury. Before each measurement, the electrode was polished by very fine emery paper and then by a soft cloth, whereby it attained a smooth bright surface. It was then rinsed with distilled water and dried with filter-paper. Electrodes B were prepared as recommended by Shoch and Brown (*J. Amer. Chem. Soc.*, 1916, **38**, 1660) by deposition on platinum plates 1 × 1·2 cm. from a solution prepared by dissolving about 0·1 g. of chemically pure trioxide and about 2 g. of hydrazine hydrochloride in 20 c.c. of pure concentrated hydrochloric acid, the solution being quickly diluted to 250 c.c. As an anode, an antimony button, prepared by reducing the purest pentoxide in sodium cyanide was used. Electrolysis was effected at 60—70°, using a current density of 0·50 amp./cm.^{2}. The process of deposition required about 6 hours, and the deposit consisted usually of bright grey minute crystals which adhered firmly to the platinum base.

Buffer Solutions.—Clark and Lubs's buffers (Clark, "The Determination of Hydrogen Ions," London, 1928, pp. 192 *et seq.*) covering the pH range 1—10 were used. Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1928, **50**, 2125), in examining their antimony electrodes in this series at 25°, questioned the validity of the temperature coefficients assigned by the respective authors; it was therefore necessary to determine the pH values of the buffers at the working temperature of 30° ± 0·02°, using the hydrogen electrode, and in buffers of pH <8 the quinhydrone electrode as well. As a reference electrode a saturated calomel half-cell was used, the E_0 pH of which was determined as in Part I. By correcting the hydrogen pressure at 30° to 728·2 mm., taking the vapour pressure of the solution at this temperature as equal to 31·8 mm., and using the relation proposed by Clark (*op. cit.*, p. 262), a correction in the measured e.m.f. values of only 0·56 mv. was introduced. Taking the mean values of several determinations, values at 30° were obtained which did not diverge from the corresponding values at 20° by more than 0·05 pH unit. The values at both temperatures are shown in Table I.

TABLE I.

pH at 20°	1·00	1·50	2·00	3·00	4·00	5·00	6·00	7·00	8·00	9·00	10·00
pH at 30°	0·95	1·45	1·95	3·00	3·99	5·00	6·01	7·01	8·00	8·99	10·01

Preparation of Materials.—The water used for recrystallisation of salts and preparation of stock solutions was twice redistilled and then boiled and cooled before use. Its conductivity was checked on different occasions and was on the average 2·5 × 10^{-6}. The sodium hydroxide was prepared and dissolved in the complete absence of carbon dioxide. The hydrochloric acid was diluted from constant-boiling acid prepared as recommended by Foulk and Hollingsworth (*J. Amer. Chem. Soc.*, 1923, **45**, 1220), and was standardised gravimetrically by way of silver chloride. The potassium chloride was purified by five crystallisations of the chemically pure product and then dried at 120° for two days. The potassium hydrogen phthalate was three times crystallised below 20° as recommended by Dodge (*ibid.*, 1920, **42**, 1655) and then dried to constant weight at 110°. Pure potassium phosphate was three times crystallised and dried to constant weight at 110°. Boric acid was three times crystallised and air-dried below 56°.

The hydrogen was prepared by electrolysis of sodium hydroxide solution between nickel electrodes and was purified as in Part I of this series.

Electrical Measurements.—These were performed in the same manner as in Part I.

Results.—(1) Consideration of the variation of potential with time for both electrodes shows that: (*a*) From the time of immersion in the unstirred solutions, the potentials become nearly steady in almost all buffers within 1—2 hours. The steady states usually persist, however, only for a further 1—2 hours, after which further drifting occurs. This continues for about 20 hours, and apparent equilibrium values are then reached which remain practically constant for several hours. (*b*) The steady-state values obtained with both electrodes approach each other closely in buffers with the same pH and are almost always higher than the corresponding apparent equilibrium values which on the whole also approach each other.

(2) By plotting the steady state values (obtained after 1—2 hours) against pH, curves are obtained (Fig. 1) which are straight lines only within the pH ranges 1·90—7·25 and 1·90—7·00 with the two types of electrode respectively. By comparing the straight portions with each other and with the theoretical plot, it is found that they possess slopes of 0·0586 and 0·0647 respectively and thus differ both from one another and from the theoretical slope (0·0601 at 30°).

(3) By plotting the apparent equilibrium values (obtained after about 24 hours) against pH, irregular curves (Fig. 2) rather than straight lines are obtained which possess, however, the same trend and run nearly parallel to each other.

DISCUSSION.

From the present data it is not possible to provide a satisfactory explanation for the irregular trend of the potential–pH curves as shown in Fig. 2 as compared with the almost straight lines shown in Fig. 1 although the potentials in the former case were apparent equilibrium values whereas in the latter they were but averaged steady states. Discussion of the above behaviour of the electrode is therefore deferred to Part IV, and only a preliminary discussion of certain matters emerging from this and other work is now attempted.

Owing to the fact that the antimony electrode does not always follow a theoretical relation, as it should if it functioned properly as a metal–metal oxide electrode, it might appear that the value of the term E_0' of any particular electrode is useless except for deriving (together with value of $\Delta E/\Delta\text{pH}$) the calibration relation on the basis of which observed e.m.f. values can be accurately converted into pH. Careful examination of available data (Table II) reveals, however, that the E_0' values assigned by the different authors, as referred to the hydrogen electrode, fall into two categories. The first comprises the majority of values, which lie within the limits 0·220—0·275 v., with most values at about 0·250 v.; and the second comprises values about 100 mv. lower, *i.e.*, at ~0·150 v. The measurements leading to the former values were mostly made in air with massive or electrodeposited metal with or without the trioxide. Those leading to the latter values were essentially the same except that finely divided metal was also involved in the electrode system used. We made some experiments following the same procedure and obtained essentially the same low E_0' values. The phenomenon was also studied in this laboratory in greater detail with arsenic electrodes, with the same results, *viz.*, two sets of values were obtained with ~100 mv. difference depending on the presence or absence of the finely divided metal. We shall report on these interesting results in a subsequent publication.

It is now desirable to find out which of these values agree with that theoretically calculated in case of the antimony electrode. There is no agreement among the different authors as to whether antimony trioxide or any other definite oxide is the one governing the mechanism of the electrode. The trioxide, being the stable oxide in contact with the metal, is probably first formed and when left in contact with air and water may undergo gradual oxidation (Wulff *et al.*, *Z. Elektrochem.*, 1935, **41**, 542) so as to become covered with higher oxides. For antimony trioxide, the free energy of the reaction $2Sb + 1\frac{1}{2}O_2 = Sb_2O_3$ is $-$ 149,030 cals. (Latimer, " Oxidation Potentials," New York, 1938, p. 109). The free energy of the reaction O_2 (gas, N.T.P.) $+ 3H_2O = 6e + 6OH'$ as computed by Lewis and Randall (" Thermodynamics," New York, 1923, p. 485) is 56,560 cals. Hence for the reaction $2Sb + 6OH' = Sb_2O_3 + 3H_2O + 6e$ the free energy change ΔF is 92,480 cals., and accordingly $E = -$ 0·688 v. at 25°.

FIG. 1.

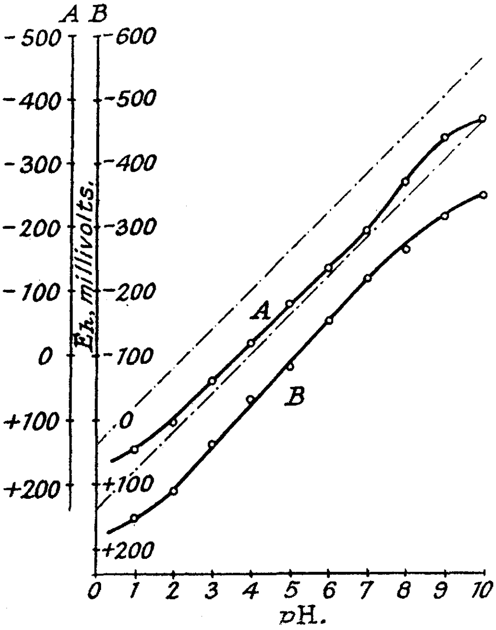
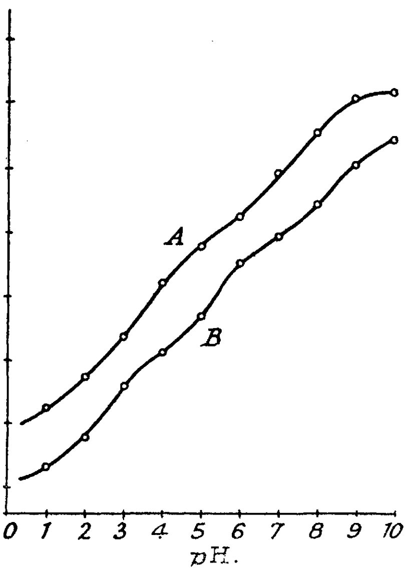


FIG. 2.



The potential of the hydrogen electrode system at unit pressure of hydrogen and unit activity of hydroxyl ion is $-$ 0·828 v. at 25°. Hence E_0' for the system $Sb–Sb_2O_3–OH$ is 0·140 v. at 25°. Similar calculations show that E_0' for the systems $Sb–Sb_2O_4–OH$ and $Sb–Sb_2O_5–OH$ is 0·338 and 0·389 v., respectively.

The above results indicate that only the experimentally found lower E_0' values are in fair agreement with that calculated for the trioxide, whereas the others are higher than this but are much lower than those calculated for the other two oxides. One cannot, however, conclude that the electrode process in the latter case is governed by the presence of a mixture of the trioxide and a higher oxide for the following reasons : (*a*) The higher E_0' values fluctuate round 0·250 v. which would require the presence of a nearly definite ratio of both oxides in all types of electrode under a wide variety of experimental conditions. (*b*) The values are derived on

TABLE II.

Ref. no.	Electrode type.	Relation assigned (hydrogen scale).		pH range.
1	Plated-metal powder	0·152 —0·05915pH	25°	Strong acid
2	Massive	0·240 —0·0485pH 0·272 —0·0536pH	14°	—
3	,,	0·231 —0·054pH	25°	1 —12
4	Metal powder on platinum	0·1512—0·0586pH 0·1513—0·0585pH	25° 25°	5 —10 2·2—10
5	Massive	0·231 —0·054pH	25°	4 — 9
6	,,	0·229 —0·057pH	26—29°	2 —12
7	Plated	(No accurate relation)		
8	Massive	0·165 —0·043pH	18°	Neutral range
9	,,	(No accurate relation)		
10	Plated	0·272 —0·053pH	14°	3 — 9
11	Massive	0·252 —0·0498pH	30°	—
12	,,	0·257 —0·053pH	14°	—
13	,,	0·251 —0·059pH	25°	2 — 7
14	,,	0·261 —0·0575pH	24°	—
15	,,	0·258 —0·0567pH	20°	2 —12
16	,,	0·249 —0·0538pH	10—25°	1 — 9
17	,,	0·269 —0·059pH	25°	2·5— 8·5
18	,,	0·237 —0·059pH	25°	1 —11
19	,,	0·262 —0·056pH	18°	5 — 7
20	,,	(No accurate relation)		
21	,,	(Electrode functioning more likely as an oxygen electrode)		
22	,,	0·248 —0·059pH 0·290 —0·051pH		3 — 7 7 —11
23	Massive	0·224 —0·0586pH		1·9—7·25
	Fresh-plated	0·220 —0·0647pH		1·9—7·00

References.—(1) Schuhmann, *J. Amer. Chem. Soc.*, 1924, **46**, 52. (2) Kolthoff and Hartong, *Rec. Trav. chim.*, 1925, **44**, 113. (3) Franke and Willaman, *Ind. Eng. Chem.*, 1928, **20**, 87. (4) Roberts and Fenwick, *loc. cit.* (5) Snyder, *Soil Sci.*, 1926, **26**, 107. (6) Lava and Hemedes, *Phillipine Agri.*, 1928, **17**, 337; *Chem. Abst.*, 1928, 2125. (7) Kolthoff and Ishimaru, " Potentiometric Titrations," New York, 1931, p. 238. (8) Brinkman and Buytendiyk, *Biochem. Z.*, 1928, **199**, 387. (9) Di Gleria, Kiserlet, and Közlemenyak, see *Chem. Abstracts*, 1931, 3271. (10) Shukoff and Awsejewitsch, *Z. Elektrochem.*, 1930, **35**, 348. (11) Harrison and Vridhachalam, *Mem. Dept. Agri. India Chem. Serv.*, 1929, **10**, 157. (12) Britton and Robinson, *J.*, 1931, 458. (13) Parks and Beard, *J. Amer. Chem. Soc.*, 1932, **54**, 856. (14) King, *Ind. Eng. Chem. Anal.*, 1933, **5**, 323. (15) Tomiyama, *J. Biochem.* (*Japan*), 1933, **18**, 285. (16) Memura and Sueda, *Bull. Chem. Soc. Japan*, 1933, **8**, 1. (17) Mehta and Kulkarni, *J. Indian Inst. Sci.*, 1935, **18***A*, 85. (18) Bravo, *Chim. e Ind.*, 1935, **17**, 521. (19) Fischbeck and Eimer, *Z. Elektrochem.*, 1938, **44**, 845. (20) Tamai, *J. Biochem.* (*Japan*), 1939, **29**, 307. (21) Kauko and Knappsberg, *Suomen Kem.*, 1939, **12***B*, 17; *Chem. Abst.*, 1939, 6726. (22) Perley, *Ind. Eng. Chem. Anal.*, 1939, **11**, 319. (23) Present investigation.

the basis of initial steady-state values, and it is plausible to assume that there has not been sufficient time for a lower oxide to be formed on the metal and then to be transformed in part into a higher oxide. This state, on the other hand, may be realised after longer periods of time but the potentials then obtained do not lead to a straight-line relationship. (*c*) Arsenic electrodes of similar types lead to similar results.

Owing to the above facts, the suggestion is made that the behaviour of massive and electrodeposited antimony electrodes in air is governed by an oxygen-overvoltage effect which is superposed upon the reversible Sb–Sb_2O_3–OH potential, making it more positive by ~100 mv. Further evidence for the theory, and the way in which this effect is brought about, is given in Part IV. Meanwhile, the following rough picture may be used to interpret the variation of potential of the antimony electrode with time. Considering electrodes A and B after immersion, it is highly probable that in the presence of water dipoles and other ions some time will be required for oxygen molecules from the atmosphere to accommodate themselves at suitable positions on the electrode surface. Since atmospheric oxidation is generally believed to involve primarily an electron transfer from the substance to be oxidised to oxygen molecules (Weiss, *Trans. Faraday Soc.*, 1938, **34**, 1053), there will arise a sort of dipole layer on the electrode surface with charged oxygen atoms on its outer side (oxygen doublets). Once this condition is approximately satisfied, the electrode process will mainly be limited to the entry and exit of electrons subject to an oxygen overvoltage, and there arises a steady state as revealed by the behaviour of the electrodes after 1—2 hours. At this stage, the electrode is neither a metal–metal oxide nor an oxygen but rather a metal–metal oxide–oxygen electrode.

The film formed is not completely impervious to metal ions, for otherwise the electrode should behave as an oxygen electrode. Local action processes by which the metal is anodically dissolved and oxygen cathodically transformed into hydroxyl ions may therefore take place, resulting in development of the metal oxide on the electrode surface. This leads in turn to a slackening of local action processes and there arises a state of apparent equilibrium as revealed by the electrodic behaviour after 20—24 hours. The development of a layer of the trioxide does not imply that the electrode will not be still governed by an oxygen-overvoltage effect. Antimony in the trioxide possesses an open structure and tends to be oxidised further in the presence of water and air. The mechanism leading to the oxidation of the metal may, therefore, still apply to the trioxide, which has been found to be transformed into the higher oxides without appreciable changes in the geometry of the crystal lattice : as shown by Simon (*Z. anorg. Chem.*, 1927, **165**, 31), the trioxide becomes denser by only about 8% when converted into the tetroxide.

The overvoltage effect observed and leading to an increase in the E_0' by ~100 mv. is in accord with the results of Langmuir's investigations on thin films on metal surfaces (*J. Amer. Chem. Soc.*, 1916, **38**, 2221), for he found that films of a gas can strongly influence the electron emission of pure metals, in the sense of a decrease when the gas is liable to be bound on the surface as negative ions, and an increase when it forms positive ions. Bowden and Rideal (*Proc. Roy. Soc.*, 1928, **120**, 59) found that it required the passage of 6×10^{-7} coulombs of electricity per cm.^{2} of accessible electrode surface, a quantity which was independent of the nature of the cathode material, in order to change the potential of the cathode by ~100 mv. at 25°. If these values in the appropriate units are substituted in the Helmholtz equation $\Delta E = 4\pi\Delta n\mu$, where ΔE is the increase in the interfacial potential resulting from the addition of Δn electric doublet of dipole moment μ to a double layer, then it is found that μ is equal to $7{\cdot}2 \times 10^{-18}$ c.s.u., which is the product of the charge of an electron and the approximate dimensions of an atom, *viz.*, $4{\cdot}77 \times 10^{-10}$ e.s.u. and $1{\cdot}5 \times 10^{-8}$ cm.

By involving the powdered metal in their electrode systems, Schuhmann (*loc. cit.*) and Roberts and Fenwick (*loc. cit.*) obtained E_0' values closely approaching the theoretical one. The fact that an electrode system in the form of a mat of the finely divided metal on bare platinum, or the mere introduction of the powdered metal together with the massive electrode, should set up the thermodynamic potential, is noteworthy. However, as far as could be gleaned from the literature, the importance of this phenomenon has never been emphasised beyond the statement made incidentally by Richards and Lewis (*Z. physikal. Chem.*, 1899, **28**, 1), who implied that the most reliable results for the normal electrode potentials of zinc and cadmium were obtained by using a mat of the powdered metal on bare platinum.

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