THE ANTIMONY-ANTIMONY OXIDE ELECTRODE¹

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C'OSTESTS

I. INTRODUCTION

Despite the fact that the general properties of the antimony-antimony oxide electrode were recognized thirty-five years ago (132), its detailed behavior is still not fully understood. In fact, the general conclusions reached by Hauke *(52)* are not very favorable to the practical use of this electrode for pH measurement, although some workers have claimed results of high precision. The object of this review is to surrey the conflicting data on the antimony electrode, the various theories of its operation, its construction, and its important properties, such as its temperature coefficient.

Earlier reviews have been given by Carreras (24) , Ball (3) , Greer (44) , and Vellenger (133, 134).

II. PREPARATION OF ELECTRODES

The three main types of antimony electrode—namely, "stick," plated, and powder--will be discussed in turn.

A. The "stick" antimony electrode

This form of electrode was used by Uhl and Kastranek (132) as an indicator electrode for the titration of acids and bases. Kolthoff and Hartong (80) preferred to add some antimony trioxide to the antimony melt before casting the electrode as a cylindrical rod. They found that equilibrium was then more quickly attained. This procedure has been adopted by other workers. Solid elec-

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trodes made by compressing finely powdered antimony are claimed to be more uniform than cast electrodes (114).

Commonly a long stick is partially immersed in the solution or a short stick is cemented into one end of a length of glass tubing, electrical connection in either case being made by means of *a* flexible copper wire soldered to the end remote from the solution. Another method for making electrical contact, viz., use of a small mercury pool joining the antimony to *a* copper lead, was found by Perley (100) to give erroneous results on continuous operation. For industrial purposes, he developed a cast antimony electrode mounted in hard rubber (102).

A modification of the stick electrode, in which only the extreme tip of the antimony is exposed, was developed by Levin (85) and is shown in figure 1. When the antimony surface is cleaned by rubbing on fine emery paper, the glass sheath breaks away gradually. Experience in our laboratory has shown that this electrode is easily constructed and behaves satisfactorily.

Microelectrodes of the stick type have been described by Kamieński and his coworkers (23, 68, 69, *TO,* 71, 72, 73, 74) and by Thompson and Brudevold (20, **122, 123).** An electrode shaped like a dental probe is shown in figure 2 (123). It is made by drawing out thick-walled Pyrex tubing. A silver wire passing through a molded joint joins the inner end of the antimony to the shielded wire leading to the pH meter. An enlarged view of the tip is shown at (a).

FIG. *2.* The dental-probe electrode

FIG. 3
FIG. 3. Electrode system with rotating brush. A, to reference electrode; B, gas inlet FIG. **4.** The powder electrode of Roberts and Fenwick

A stick electrode in a syringe-like protective mantle has been described by Schollenberger (112).

To maintain a clean electrode surface, scraping (10) or brushing (81, 107, 145) may be used. **A** typical arrangement is shown in figure **3** (145). The polishing of an antimony electrode by surrounding it with an abrasive substance is the subject of a Japanese patent (126).

In many cases the electrodes have been cast from commercially available C.P. antimony. In a study of nearly fifty electrodes using antimony from three different sources (including "Commercial Lump"), Ball *(3)* stated that the polished electrodes usually did not differ in potential by more than 4 to 5 mv., whether annealed or not. On the other hand, Shcherbakov (115) found that only electrodes made from very pure metal gave reproducible results. When

purification has been attempted, this has normally been done by electrolysis from a fluoride medium (see, for example, references *53,* 85, 109, 113, 115).

B. The plated antimony electmde

Brinkman and Buytendiyk (18) found that a pure antimony electrode was not suitable for the determination of the pH of blood. They therefore used a deposit of this metal on a platinum wire. Zhukov and Avseyevich (148) plated antimony onto a thin layer of mercury previously deposited on a platinum wire. They used a solution of antimony trichloride in dry acetone. The antimony amalgam which is first formed becomes covered with a fine crystalline layer of antimony. These two workers later studied the deposition of antimony from the trichloride dissolved in a variety of organic solvents *(2).* **A** steady potential was obtained only if the deposit ms of the grayish matte type. Solutions in formic acid, acetonitrile, and nitrobenzene gave smooth deposits but unsteady potentials. Methanol is less satisfactory than acetone. Böttger and Szebellédy (12) examined various earlier forms of electrodes and described an antimonized antimony electrode which required 5 min. or less to reach a constant value.

Gysinck (47) found that antimony deposited electrolytically on platinum wire lost reproducibility. Pieper (104) used antimony plated on platinum and on copper for electrodes in acid-base titrimetry.

Deposition from aqueous hydrochloric acid solution containing hydrazine (111) has been used by several workers (128, 139). Antimony is deposited on platinum plates at a temperature of $60-70^{\circ}\text{C}$, using a current density of 0.50 amp./cm.² DiGléria (33) has described an electrode prepared by electrodeposition upon a base of tin-plated copper.

C. *Electrodes employing antimony powder*

The electrode vessel shown in figure 4 was used by Roberts and Fenwick (109) in their classic investigation of acidity measurements with the antimony-antimony oxide electrode. This is similar to an earlier version (108) but arranged for use with nitrogen. It is a modification of the type described by Brgnsted, in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, and out to the liquid junction. Electrode **A** is of platinum, which in some experiments carried a thin plating of antimony. In other cases, the electrode was treated with antimony trifluoride solution to adjust the potential of the wire electrode to that of antimony. B is a column of antimony crystals, prepared by the method of Schuhmann (113), using cotton plugs to prevent clogging of the stopcock and to break the column into several sections. This allows rapid flow of electrolyte for washing and assists in attainment of equilibrium. In other experiments, the column was a mixture of antimony and highly purified antimony trioxide powder. When necessary, nitrogen is introduced at C and escapes at D.

A simple powder electrode system shown in figure 5 has been described by Holmqvist (59), who found that the potentials of antimony rods are very different from those of antimony powder (58). El Wakkad (139) employed commer-

FIG. **5.** The Holmqvist powder electrode system

FIG. *6.* Rate of flow apparatus. **A,** the antimony needle electrode; B, the buffer reservoir; C, measuring cylinder; D, to reference electrode.

cially available antimony powder and found that although pseudo-equilibrium was attained within **3** to 6 hr., a period of 120 to 144 hr. was necessary to obtain steadier values.

Certain other antimony electrodes have been used which do not fit rigidly into the classifications given above. Böttger and Szebellédy (12) investigated the properties of electrodes consisting of antimony alloyed with bismuth and cadmium (49) and a platinum electrode covered with "explosis'e'' antimony **(29).** All required 10 to *25* min. to reach a constant value, as opposed to the *5* inin. required for the antimonized antimony electrode mentioned above. Antimony coated vith sulfide instead of oxide may be used to determine the saponification value of oils (4) , but offers no advantage over the ordinary antimony electrode. In his measurements made both under load and under overcompensation, Mantzell (87) used a ring antimony electrode having a surface of 25 cm^2 . Novák (95) has studied various bimetallic electrode systems in which one element was antimony.

111. ELECTRODE PRETREATMENT

Where employed, electrode pretreatment may be classified as acidic, alkaline, or electrolytic. Togel (137) used stick electrodes which had been dipped in concentrated nitric acid. The "etched" electrode of Böttger and Szebellédy (12) is prepared by successive treatment with dilute sulfuric and nitric acids.

Treatment with a hot solution of sodium hydroxide (148) or immersion for several days in a solution of pH 11.8 (125) is an example of alkaline pretreatment. The anodic dissolution of antimony in alkaline medium has been studied by Grube and Schweigardt (45) .

Anodic polarization in dilute sulfuric acid is claimed to give a reproducible, stable electrode of the plated type *(2).* Electrolysis in sodium carbonate solution *(53)* or brief anodizing (3, discussion) have also been used. El Wakkad and Hickling (140) have made an oscillographic study of the anodic behavior of antimony in both acid and alkaline solutions. For the continuous recording of the acidity of human gastric contents, treatment with bromine water was used (48).

In many cases, however, no pretreatment, other than washing or polishing with fine emery paper, was used (see, for example, references 97, 126, 139). However, Shcherbakov (115) stated that polishing with fine emery gives differences of up to 10 mv. After cleaning the electrodes with emery, King (79) stood them in water to undergo slight oxidation. He reported that accuracy and reproducibility were increased if the electrode was "tarnished."

IV. RELATIONSHIPS BETWEEN E.M.F. AND PH

Although it is generally agreed that the antimony-antimony oxide electrode is a suitable indicator in acid-base titrimetry, the position of this electrode as a means for the accurate determination of pH is far less satisfactory. Linear E.M.F.-pH relationships of the type:

$$
E = a + b \text{ pH} \tag{1}
$$

TABLE 1

Relationships between E.M.F. *and pH with antimony-antimony oxide electrode*

The values a and *b* are referred to equation *1.*

t Values extrapolated from the author's curve.

have been reported by numerous workers; examples of these are listed in table 1. Noteworthy are the following points: (i) there is great variation in the a term (due allowance having been made for the differing reference electrodes); *(ii)* the values of the slope or *b* term differ; *(iii)* in very few cases has the *b* term a value fairly close to the "theoretical" value, e.g., 0.05915 at 25°C ; *(iv)* the value of the *b* term is sometimes different under acid and alkaline conditions; and *(v)* the range of applicability varies considerably.

DiGléria $(32, 33)$ stated that no linear relationship exists between the potential and the pH, while Yoshimura (146) could not obtain a general calibration curve applicable to differing experimental conditions. On the other hand, numerous other workers (12, 13, 47, 50, 65, 136, 132) agree with those referred to in table 1 that a linear relationship exists.

Several authors have reported that in addition to a change in slope (see table 1), a "kink" appears on the $E.M.F.-pH$ curve. This "kink" occurs between the two linear portions (13, 47, 65).

V. TEMPERATURE COEFFICIEST

An extensive study of the temperature coefficient of the plated type of antimony electrode was made by Avseyevich and Zhukov (2). They showed that both *a* and *b* (see equation 1) were temperature-sensitive. Their final equation, as corrected by Ball (3), then becomes:

$$
pH = \frac{E - 0.01 - 0.00025(t - 18)}{0.0542 + 0.000275(t - 18)}
$$

where *t* is the temperature in ${}^{\circ}C$, and *E* is the potential against the normal calomel electrode. A similar equation was also obtained for use with the saturated calomel electrode. Bravo (15) also studied the variation with temperature of the two quantities a and *b* in a variety of buffered salt solutions.

Table 2 contains the temperature coefficients reported by several other workers. Part of the variation in reported temperature coefficient is, of course, due to

Electrode Type	Reference Electrode	Millivolts per °C.	pH Range	Temperature Range	Reference
				\circ C.	
Plated		0.5	Neutral		(18)
Stick		1.3	(Soils)		(34)
Stick	SCE	1.5	11		(55)
		1.5	$2 - 4$		
$Stick$	NCE	2.0	$5 - 7$	$10 - 30$	(125)
		$2.5 - 3.0$	$8 - 11$		
$Stick$	SCE	3.3		$25 - 40$	(89)
		1.15	3		
Stick	SCE	2.1		$15 - 45$	(101)
		3.44	12		
		-1.3	≤ 4		
Stick	0.1 NCE	Intermediate	$4 - 7$	$20 - 50$	(107)
		-2.3	>7		

TABLE *2*

Temperature coeficients with the antimony-antimony oxide electrode

the use of differing reference systems. According to Perley (101), the temperature coefficients for buffered and unbuffered solutions are different.

Other data concerning temperature coefficients have been given (38), some indicating the dependence of this quantity on pH (21, *30).* Puri (106) claimed that the effect of temperature on the E.M.F. can be largely eliminated by replacing the usual calomel half-cell with a standard antimony electrode. Cells involving two antimony electrodes have been used by other workers $(43, 135)$.

VI. INTERFERENCES

A. The e\$ect of oxygen

Using a slowly flowing, air-free electrolyte saturated with cubic antimony trioxide, Roberts and Fenwick (109) found that the potential of their antimony electrode was a linear function, with theoretical dope, of the pH of the solution. However, equal accuracy was secured without exclusion of air if standardization with solutions of known acidity was employed. On the other hand, Franke and Willaman (41) found that the antimony electrode was adversely affected by oxygen or carbon dioxide; reproducible pH results have been obtained when carbon dioxide was excluded (118). **A** potential shift obtained with both the antimony and the quinhydrone electrode was attributed to absorption of atmospheric carbon dioxide (67).

The bulk of the measurements with the antimony electrode have been carried out in air-containing solutions. Tourky and Mousa (128) have examined its behavior out of contact with air, while Gysinck (47) has recommended that the solutions be covered with paraffin oil to protect them from air.

It has been shown that in suspension, antimony easily undergoes surface oxidation on the passage of air (90) and that in aerated water larger amounts of antimony are dissolved than would correspond to the solubility equilibrium of antimony trioxide (28) . The product formed on an antimony electrode in contact with air and water markedly affects the potential, as does the partial pressure of oxygen **(145).** The potential is stated to change with the oxygen pressure in accordance with the theoretical requirement of an oxygen electrode but not to be affected by hydrogen or nitrogen gas *(77).* To obtain reproducible results in continuous pH measurements, Shcherbakov (115) found that the solution had to be saturated with air of a constant partial pressure of oxygen. Holmqvist (59) showed that with solid electrodes the potential is affected by the formation of hydrogen peroxide; use of antimony powder decomposes this substance. Erratic results obtained in determinations of the pH of soils were attributed to deficiency of dissolved oxygen in the suspensions (112) .

Perley (101) has studied the effect of the concentration of dissolved oxygen on the $E.M.F.-pH$ relationship of the antimony-saturated calomel electrode system. For example, in a presaturated and constantly stirred buffer of pH 6.91 at 25[°]C., the saturating gases gave the following results: nitrogen, 0.460 v.; air, 0.398 **v.;** and oxygen, 0.375 v. He pointed out that tendency toward instability in the acid range when the dissolved oxygen concentration is low and failure to follow the Nernst equation in the alkaline range when dissolved oxygen is present are characteristic of the antimony electrode.

B. The e\$ect of *stirring*

According to Brinkman (17), the antimony electrode gives reproducible readings in the neutral region if the liquid is not moving or streaming. Absence of stirring has been recommended by various other workers (see, for example, references 15, 97, 134). On the other hand, Britton and Robinson (19) found that vigorous mechanical stirring \vas necessary to obtain steady readings. Gysinck (47) claimed that best results were obtained if the stirring was not too rapid. In the examination of soil suspensions, a rotating electrode improved reproducibility (61) . Many other workers recommend either stirring or shaking.

Harrison and Vridhachalam (51) noted that potentials in unstirred solutions were somewhat higher than those in stirred solutions. Tomiyama (125) reported that on suddenly stirring the solution, the potential increases on the acid side and diminishes on the alkaline side.

X clue to these conflicting results was afforded by the work of Fischbeck and Eimer (38) , who used the apparatus shown in figure 6 to study the effect of movement of the liquid. They showed that when the solution moves past the antimony electrode, the potential at first changes rapidly then soon approaches an approximately constant value. This is illustrated in figure **7** and refers to the movement of a pH 6.81 phosphate buffer in a tube of 4.5-mm. bore. The effect of agitation has been extensively studied by Perley (101). With solutions saturated with oxygen, the difference between agitated readings did not exceed 0.1 pH unit over the entire range 4 to 11.

C. *Chemical interferences*

Although fairly reproducible results have been obtained in the presence of mild oxidizing or reducing agents (101), the presence of these agents normally causes difficulty (7, 19, 38, 78). Furthermore, it is well known that certain com-

FIG. **7.** The effect of rate of flow on potential

plexing agents, notably hydroxy acids, such as citric (3, 4, 5, 10, 88, 107, 121, 149), and certain of the amino acids (5), give erroneous results.

Metals which can be replaced from solution by antimony give trouble even at low concentrations (101). Thus it is not surprising that Burlachenko (21) did not obtain good results with the antimony electrode in solutions of copper salts. In fact, the presence of 0.5 p.p.m. of copper caused an immediate error of 0.2 pH in a nearly neutral buffer (101). Further, the spontaneous deposition on an antimony surface may be used for isolating traces of copper prior to its colorimetric determination (103). Freshly precipitated ferric hydroxide in soil suspensions does not affect the accuracy of the antimony electrode (94).

Itano and Arakawa **(63)** found that the antimony electrode could be used for the determination of the acidity of soils and waters containing hydrogen sulfide. On the other hand, Pleass (105) examined the behavior of glass and antimony electrodes in tannin solutions; he found that in the presence of sulfides or sulfites only the glass electrode gave good results. It is claimed that the presence of sulfur dioxide in sugar factory products (25) and in pulp mill liquors (41) does not affect the functioning of the antimony electrode.

Apart from the above specific instances, it is well established that the nature and concentration of the solution have a bearing on the potential (10,46, 79, 146). Bravo (15) investigated the behavior of the antimony electrode in the presence of variable amounts of common sodium and potassium salts. Brudevold and Thompson (20) found that phosphate ions had no appreciable effect on the potential and that calcium chloride had no effect up to concentrations of 1 molar. Likewise gelatin and agar (3 per cent) did not affect the results (118).

VII. THEORIES OF ELECTRODE BEHAVIOR

Ignoring activity effects and assuming that the potential (π_{Sb}) of an antimony electrode at 25° C. is controlled by the following equilibria:

$$
Sb(s) = Sb^{+++} + 3e^-
$$
 (3)

and

$$
Sb_2O_3(s) + 3H_2O = 2Sb^{+++} + 6OH^-
$$
 (4)

it is easily shown that:

$$
\pi_{\rm sb} = \pi_0 + 0.05915 \left\{ \text{pH} - \frac{1}{6} \log \left[\text{Sb}_2 \text{O}_3 \right] + \frac{1}{2} \log \left[\text{H}_2 \text{O} \right] \right\} \tag{5}
$$

If the last two terms are disregarded, π_0 should thus be the difference in potential between an antimony-antimony trioxide electrode and a hydrogen electrode immersed in the same solution (109). Measurements by Schuhmann (113) on this cell system showed that in acid solution tervalent antimony is present mainly as SbO⁺. Various other ions, e.g., $SbO₂$, may also exist under certain conditions, but if the system is in equilibrium, equation *5* will hold regardless of the ionic species containing antimony (109). Roberts and Fenwick pointed out that unless the antimony trioxide is in its standard state, the appropriate term in equation *5* does not vanish. They obtained their beat results with cubic antimony trioxide.

According to Parks and Beard (98), the antimony trioxide is present as an adsorbed film, the electrode reaction occurring at the metal-metal oxide interface. Deviations in extreme acid and alkaline solutions were attributed to the formation of SbO⁺ and SbO₂ in the oxide film (99). Mehta and Kulkarni (89) have claimed that the pH response of cast antimony is due to antimony tetroxide $(Sb₂O₄)$ dissolved in the metal.

Wulff, Kordatzki, and Ehrenberg **(145)** showed that, in contact with air and water, continuous oxidation of the antimony electrode occurred, a product showing peroxide properties being formed (see, also, references *58,* 59, GO, 138, 144). They concluded that the oxidation process and diffusion of the reaction products govern the electrode potential.

Fischbeck and Eimer (38) developed a theory based on oxidation-reduction equilibria and pointed out that the behavior of antimony was in many respects similar to that of platinum. Spychalski (118) agreed with the analogy with platinum when the antimony electrode is under reducing conditions. However, under conditions favorable for oxide formation, the behavior is stated to be that of an irreversible electrode of the second order. Kauko and Knappsberg (76, *77)* calculated the dissociation pressures of the oxides of antimony and considered the data to favor the view that antimony behaves as an oxygen rather than a hydrogen electrode.

Tourky and Mousa (128) have pointed out that the π_0 values" (see table 1) fall into two categories: namely, values lying within the approximate limits 0.22 to 0.28 v. and those 100 mv. lower. These potentials are referred to the normal hydrogen electrode, whereas the data in the table give the reference electrode of the original authors. Tourky and Mousa calculated the thermodynamic π_0 value" as 0.140 v. against the normal hydrogen electrode and concluded that measurements approaching this value were obtained only when finely divided metal was used in the electrode system. The behaviors of the stick and plated antimony electrodes were explained by postulating the existence on the surface of oxygen doublets which gave rise to an oxygen overvoltage effect (129). This is superimposed upon the reversible $Sb-Sb₂O₃-OH⁻$ potential, shifting it by about 100 mv. Once this doublet layer is formed, there is a steady stage at which the electrode is neither a metal-metal oxide nor an oxygen electrode but rather a metal-metal oxide-oxygen electrode. This arises 1 to 2 hr. after immersion. Surface formation of metallic oxides causes the development of a state of apparent equilibrium after about **20** hr. Similar observations were made with arsenic electrodes. From solubility determinations, the isoelectric point of antimony trioxide was found to be pH 8.6 (130).

El Wakkad (139), on the other hand, considers that when equilibrium is reached, the " π_0 value" corresponds to the reversible value of the system Sb_2O_3 - $Sb₂O₄$, and that the antimony electrode then acts as a true metal-metal oxide one. The rate of attainment of equilibrium depends upon both the supply of oxygen and the surface area of the electrode. Other workers also state that the presence of Sb_2O_4 may account for the varying behavior of the antimony electrode (14).

It appears that the behavior of the antimony electrode is still not fully under-

stood. Although it can be used for routine work, results in line with theoretical considerations can be obtained only with elaborate precautions such as by the use of a carefully equilibrated powder system. The antimony electrode has recently become important both as a reference and as an indicator in nonaqueous tritrimetry. Fundamental studies of its behavior in nonaqueous systems are under way in this laboratory.

VIII. APPLICATIONS

The antimony-antimony oxide electrode has found considerable use in the study of soil acidity *(5,* 9, **33,** 34, 50, 51, 56, 57, 61, 62, *63,* 79, 84, 86, 94, 106, 112, 117, 147). In a report comparing the behavior of the hydrogen, quinhydrone, and antimony electrodes, the antimony electrode was not proved reliable (55). Magnesium may be titrated with standard potassium hydroxide *(6-4).* If present in upwards of four times the amounts of magnesium, calcium causes an error of over *5* per cent.

An electrode of the plated type was used by Brinknian and Buytendiyk (18, 22) for the determination of the pH of blood. However, they found it necessary to standardize the electrode with buffer mixtures. The conclusion of later workers is that the various types of antimony electrode are unreliable in this field (40, 127, 141, 146). The antimony electrode has also been used for gastric research (36), including the continuous recording of the acidity of human stomach contents (48). In the latter case, the electrode n-as only *5* nim. long and 1 mm. in diameter. Attached to a fine rubber tube containing the leads, it could be smallowed without any difficulty. Antimony microelectrodes have been used for dental studies (20, 91, 122, 123). From a comparison of the glass, antimony, and quinhydrone microelectrodes, Charlton (26) concluded that the glass microelectrode is the most accurate for use in the mouth.

Perley (100, 101, 102) has discussed the industrial aspects of the antimony electrode. It has been repeatedly recommended for use in sugar technology *(25,* 42, 81, 82, 124). Beretta **(7)** has stated that above pH 8 or in the presence of reducing sugars, the readings are not exact. The antimony electrode has been used satisfactorily for measuring the $\rm pH$ of natural waters (66), and factors concerning its suitability for pH determination in sea water (88) and brine (1) have been studied. The merits and applications of this electrode in the measurement of the pH of dye (31, 96) and plating (16) baths have been described. It has also been used in the latex (30), oil *(83),* soap (143), tanning (11, 105), and sulfate pulping industries (116) .

Examples of the many uses of the antimony electrode in potentiometric titrations are for the determination of iron and aluminum (75), the examination of superphosphate solutions (137), and the determination of certain local anesthetics *(37),* of cholinesterase (92), and of the oxy acids of selenium and tellurium (19). Cheshko (27) has studied the acidic properties of benzenesulfonamide, while Szabó, Csányi, and Kávai (120) have examined the interaction of aluminuni and hydroxy1 ions. The electrode has also been employed in the microtitration of "formol" nitrogen (110) and is reported to be suitable for the titration of carbon dioxide in water (150) and of acid mixtures in nonaqueous

solvents (6). The applications in the nonaqueous field have been reviewed recently (119).

pH meters involving an antimony electrode $(8, 93)$ and a mounting for this electrode (39) have been described.

"Dead-stop" titration of acids and bases using antimony electrodes has been attempted (35) .

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