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THE STICK ANTIMONY ELECTRODE FOR THE MEASUREMENT OF HYDROGEN ION CONCENTRATION⑴

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The usual hydrogen electrode method is undoubtedly the most accurate one of all the electrometric ways of estimating hydrogen ion concentration, but it cannot be applied to solutions containing reducible substances like ammine complex salts. We have already studied the above solution by using the quinhydrone electrode, but even in the limited range of its applications, our purpose was not attained. And, metal electrodes can be presented to these very reducible solutions for the determination of hydrogen ion concentration (pH). Several types of antimony electrode are thus reported for this purpose: Plated type, by Shukov and Aveyevich⑵, and Dropping type, by Roberts and Fenwick⑶. Franke and William⑷, Snyder⑸, Vlès and Vellinger⑹, Itano⑺, Parks and Beard⑻ are the principal investigators on the stick antimony electrode which has been favored because of its ease of preparation and use.

The experimental formulas given by these authors have a tolerable accuracy in their own studies, but it is difficult to find the uniformity in their results. When one wishes to determine pH values by using the antimony electrode, one must fully calibrate the metal electrode. Supposing that the disagreement of data is due to the different nature and treatment of the electrode, we have paid attention to the manipulation of the metal and principally adopted Vlès-Vellinger's idea of experiments.

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(1) Read before the 8th Annual Meeting of the Japanese Association for the Advancement of Science (Nippon Gakujutsu-Kyôkai), held at Nagoya, Japan, October 16th, 1932.

(2) Shukov and Aveyevich, *Z. Elektrochem.*, **35** (1929), 349; **37** (1931), 771.

(3) Roberts and Fenwick, *J. Am. Chem. Soc.*, **50** (1928), 2125.

(4) Franke and William, *Ind. Eng. Chem.*, **20** (1928), 87.

(5) Snyder, *Soil Science*, **26** (1928), 107.

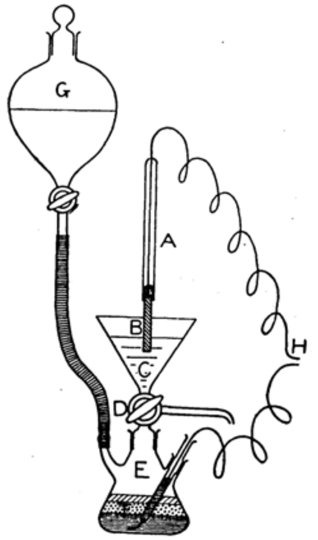
(6) Vlès and Vellinger, *Arch. phys. biol.*, **6** (1927), 38 and 92.

(7) Itano, *Ber. Ohara Inst. landw. Forsch. Japan*, **4** (1929), 273.

(8) Parks and Beard, *J. Am. Chem. Soc.*, **54** (1932), 856.

Experimental.

Apparatus. For the present determination of pH values, we have used the mode of glass vessel presented by Vlès and Vellinger⁽⁶⁾.



A : Glass tube for protecting the antimony electrode.
B : Antimony electrode.
C : Sample for determing pH value.
D : Three way stopcock.
E : Saturated potassium chloride solution.
F : Calomel electrode.
G : Reservoir for potassium chloride solution.
H : To potentiometer.

Fig. 1.

Dimension:	Diameter of glass funnel....................	6 cm.
	Height of glass funnel......................	6 cm.
	Diameter of glass vessel (bottom)............	5.5 cm.

Preparation of the Stick Antimony Electrode. A hard glass tube (about 7 mm. in inside diameter and 30 cm. in length) is filled with metallic antimony pieces to occupy at first from 10 to 15 cm. in length; and, held horizontally it is gently heated on a fish-tail formed Bunsen burner. When the antimony is sufficiently fused, the tube must be slowly moved to and fro to expel the air-bubbles in the metal. Next, the red-heated glass tube containing the fused antimony is drawn to keep a uniform diameter of about 4–5 mm., and is thrown into water for sudden cooling. If cooled gradually, in this case, the solidified antimony easily gets a cleavage surface along its cross section of the stick and becomes very brittle. To connect a copper wire with the prepared antimony stick, we apply direct electric current (70 volts; 2–3 amperes), taking the wire as cathode and the metal, as anode. We thus make an arc between the electrodes, and when the end of the stick is sufficiently fused the wire is strongly put into the fused stick of antimony. As the joint of these two metals falls easily apart, even after it was completely cooled, we generally cover the electrode with a glass tube and its end is sometimes sealed with paraffine, de Khotinsky cement or bakelite varnish.

Different Treatments of Antimony Electrodes. According to the Vlès-Vellinger's publications(6), the antimony electrode is influenced by different treatments, such as polishing with emery paper of various degrees. To study these effects more minutely, we have chosen several samples of electrodes variously prepared.

A-electrode: Compact surface polished with No. 0000 emery paper.
B-electrode: Compact surface polished with No. 00 emery paper.
C-electrode: Surface not compact, (air-bubbles are leaving mark on the surface) polished with No. 00 emery paper.
D-electrode: A-electrode containing a minute quantity of copper(9).
E-electrode: B-electrode containing a minute quantity of copper(9).
F-electrode: Polish with No. 00 emery paper and take the electrode as anode (platinum as cathode) and electrolyse water (acidified with a very small quantity of dilute sulphuric acid) from 2 to 3 minutes. Gray coloured.

All these electrodes, once polished, are again cleaned in distilled water, wiped with absorbent cotton and used.

Original Impurities detected in Antimony Pieces. We have used two kinds of antimony pieces for our present studies; one is of Japanese origin (labelled Kojima's Deer brand—Extra pure, Tokyo). By an application of the electric arc spectral method, we have detected some lines of foreign elements, thus:

Arsenic: 2349.88 Å, 2898.86 Å, 3860.60 Å
Copper: 4022.88 Å, 4062.91 Å
Lead: 3639.72 Å, 3683.62 Å
Tin: 3034.25 Å, 3175.16 Å, 3262.50 Å

Our second sample used for the preparation of the following two electrodes is the Merck's reagent where any lines of impurities can not be found, except those of arsenic.

a-electrode: Compact surface polished with No. 0000 emery paper, and left in water for more than one hour.
b-electrode: Compact surface polished with No. 0000 emery paper.

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(9) About 0.1–0.01% of copper.

Buffer Solutions. We have prepared the folowing buffer solutions, whose pH values are defined by hydrogen electrode, to observe the accuracy of our stick antimony electrode.

pH	
1.25	(50 c.c. M/5 KCl; 64.5 c.c. M/5 HCl, dilute to 200 c.c.)
1.96	(50 c.c. M/5 KCl; 10.6 c.c. M/5 HCl, dilute to 200 c.c.)
2.97	(50 c.c. M/5 KH Phthalate; 20.32 c.c. M/5 HCl, dilute to 200 c.c.)
3.97	(50 c.c. M/5 KH Phthalate; 0.40 c.c. M/5 NaOH, dilute to 200 c.c.)
4.99	(50 c.c. M/5 KH Phthalate; 23.85 c.c. M/5 NaOH, dilute to 200 c.c.)
6.05	(50 c.c. M/5 NaH_2PO_4; 5.70 c.c. M/5 NaOH, dilute to 200 c.c.)
7.07	(50 c.c. M/5 NaH_2PO_4; 29.63 c.c. M/5 NaOH, dilute to 200 c.c.)
7.99	(50 c.c. M/5 H_3BO_3, M/5 KCl; 3.97 c.c. M/5 NaOH, dilute to 200 c.c.)
9.00	(50 c.c. M/5 H_3BO_3, M/5 KCl; 21.30 c.c. M/5 NaOH, dilute to 200 c.c.)
9.99	(50 c.c. M/5 NaH_2PO_4; 46.80 c.c. M/5 NaOH, dilute to 200 c.c.)
10.59(10)	(100 c.c. Glycocoll solution(11); 50 c.c. M/5 NaOH, dilute to 200 c.c.)
12.39(10)	(80 c.c. Glycocoll solution(11); 60 c.c. M/5 NaOH, dilute to 200 c.c.)

The above mentioned buffer solutions are chosen in every one pH range and the chemicals used for the preparation have nearly the purity of reagents of the Kahlbaum's grade.

The Measured Electromotive Force (E.M.F.) Values. Table 1 shows that A- and B-electrodes, and D- and E-electrodes have respectively similar values while C- and F-electrodes show slightly different results from those of the former two pairs.

TABLE 1.

pH	Electrodes (Japanese origin)					
	A-	B-	C-	D-	E-	F-
1.25	65.3	67.7	73.0	66.0	65.8	63.2
1.96	106.7	105.5	107.5	105.7	105.5	108.4
2.97	162.5	161.6	161.6	158.5	159.5	158.9
3.97	212.2	211.3	212.8	211.6	212.8	210.6
4.99	267.9	268.5	269.1	266.9	267.7	266.7
6.05	329.6	329.6	330.9	329.8	328.0	326.8
7.07	383.4	382.0	383.7	382.7	383.0	382.1
7.99	428.3	428.1	430.6	427.6	427.8	427.1
9.00	473.9	474.9	476.5	476.5	476.7	475.4
9.99	524.3	522.8	525.6	524.4	525.9	525.7
10.59	557.0	556.0	557.6	557.5	556.5	555.9
12.39	687.0	687.1	694.7	686.0	687.1	682.6

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(10) The last two solutions are mixed according to the Sörensen's indication, while the others are based on Clark and Lubs' standards.

(11) Our glycocoll (glycine) solution is prepared by dissolving 1.501 gr. glycocoll and 1.71 gr. NaCl in 200 c.c. H_2O.

Now, A- and B-electrodes, which have almost the same surface condition, have received a different mechanical treatment, and D- and E-electrades are also polished with emery paper of different degrees, but to each is added a small and equal quantity of copper. And, the result given by these two pairs of electrodes shows that any mechanical treatment influences but slightly the E.M.F. values, while the surface condition and the chemical nature of the electrodes cannot be neglected for the measurement of E.M.F.

Our second results obtained from the electrodes prepared by the Merck's reagent are as follows:

TABLE 2.

pH	Electrodes		pH	Electrodes	
	a–	b–		a–	b–
1.25	79.8	80.5	7.03	403.4	404.7
1.99	112.1	112.1	7.93	435.8	438.0
2.99	159.0	159.2	8.91	492.5	491.3
3.97	223.3	223.3	10.05	553.4	552.4
4.99	283.0	283.3	10.77	595.3	591.8
5.95	339.8	335.0	11.97	693.5	697.9

Table 2 also shows that the slight difference of mechanical treatment has very little effect on the E.M.F. values.

Next, we have found the mean of observed values that nearly coincide with each other and have tabulated them in Table 3, comparing the calculated values from our empirical equation (see page 6–7) deduced from the experimental results.

TABLE 3.

pH	Mean values of				pH	Mean values of	
	A–B (obs.)	A–B (calc.)	D–E (obs.)	D–E (calc.)		a–b (obs.)	a–b (calc.)
1.25	66.5	66.6	65.9	65.4	1.25	80.2	71.8
1.96	106.1	104.8	105.6	103.8	1.99	112.1	113.2
2.97	161.9	159.1	159.0	158.2	2.99	159.1	169.2
3.97	211.8	212.9	212.2	212.2	3.97	223.3	224.1
4.99	268.3	267.8	267.3	267.3	4.99	283.2	281.2
6.05	329.6	324.7	328.9	324.6	5.95	337.4	335.0
7.07	382.7	379.7	382.9	379.7	7.03	404.0	395.5
7.99	428.2	429.2	427.7	429.3	7.93	436.9	445.9
9.00	474.4	483.5	476.6	483.9	8.91	491.9	500.8
9.99	523.6	536.8	525.2	537.3	10.05	552.9	564.6
10.59	556.5	569.0	557.0	569.8	10.77	593.6	604.9
12.39	687.1	665.9	686.9	666.9	11.97	695.7	672.1

Theoretical.

Many authors⁽¹²⁾ mention the theoretical side of the antimony electrode, and some of them declare that chemical changes occur on the surface of the metallic electrode, and they even give several constitutional formulas of intermediates which are supposed to be obtained. Assuming any metallic oxide whose solubility is very small, the next equation will be formed in the solution, and it shows that the metallic ion concentration of the solution is controlled by its hydrogen ion concentration.

$$MO+2H^+ \rightleftarrows M^{++}+H_2O$$

M is, in this case, a divalent metal whose oxide is therefore MO. Supposing MO nearly insoluble, then we may have

$$[M^{++}]=K[H^+]^2 .$$

Applying the Nernst equation,

$$E=e_0+\frac{0.0577}{2}\log[M^{++}]$$

Putting $K\ [H^+]^2$ in place of $[M^{++}]$,

$$E=e_0+\frac{0.0577}{2}(\log K+\log[H^+]^2) ,$$

$$E=e_0'+0.0577\log[H^+] ,$$

$$E=e_0'-0.0577\,\mathrm{pH}\quad(\text{at }17^\circ\text{C}) .$$

From this, we conclude that the electrode potential (E) can be varied according to pH value. It goes without saying that this conclusion holds only when the small solubility of the metallic oxide is realised, and the equation is similarly derived in the case of a trivalent metallic oxide of very small solubility. One of the few metals that fulfill these conditions is antimony.

Applying the principle of least-square method, we have derived the following empirical equations from each set of the experiments whose data of E.M.F. have already been tabulated.

(1) Equation derived from the mean values of A- and B-electrodes (see Table 3) ;

$$E=53.8\,\mathrm{pH}-0.7 \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\quad (1)$$

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(12) loc. cit.

(2) Equation derived from the mean values of D- and E-electrodes (see Table 3) ;

$$E = 54.0\,\mathrm{pH} - 2.1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{2}$$

(3) Equation derived from C-electrode (see Table 1) ;

$$E = 54.0\,\mathrm{pH} + 0.3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{3}$$

(4) Equation derived from F-electrode (see Table 1) ;

$$E = 53.8\,\mathrm{pH} - 1.8 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{4}$$

(5) Equation derived from the mean values of a- and b-electrodes (see Table 3) ;

$$E = 56.8\,\mathrm{pH} + 1.8 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{5}$$

With the theoretical values calculated from these empirical formulas and the observed results, we can make a diagram that represents the relation of pH and E.M.F. Of the two straight lines in the following

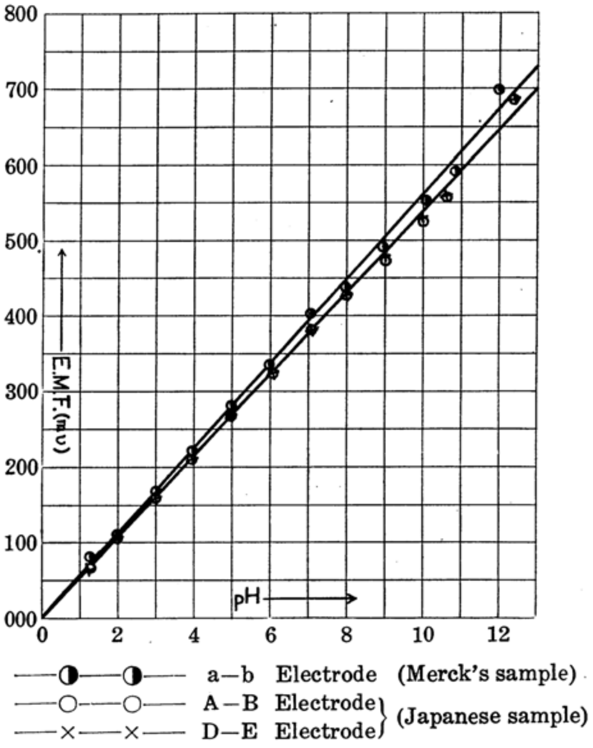

Fig. 2.

diagram (Fig. 2), the upper one shows the theoretical values deduced from the equation (5), obtained from the electrode of Merck's sample; the lower one shows the equations (1) and (2).

Next, in Tables 4 and 5, we give the maximum deviation of observed and calculated values of E.M.F. which are obtained from equations (1), (2) and (5); a percentage of the error, and the difference due to the determination of pH by hydrogen and antimony electrodes.

TABLE 4.

A-, B-, D- and E-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)		% of error from calc. value		pH—diff. (Sb to H_2)	
	A-; B-	D-; E-	A-; B-	D-; E-	A-; B-	D-; E-
1.25	−1.3	+0.6	2.0	0.9	0.02	0.01
1.96	+1.9	+1.9	1.8	1.8	0.04	0.04
2.97	+3.4	+1.3	2.1	0.8	0.06	0.02
3.97	−1.6	±0.6	0.8	0.3	0.03	0.01
4.99	+0.7	±0.4	0.3	0.2	0.01	0.01
6.05	+3.9	+4.2	1.2	1.3	0.07	0.08
7.07	+3.7	+3.3	1.0	0.9	0.07	0.06
7.99	−1.1	−1.7	0.3	0.4	0.02	0.03
9.00	−9.6	−7.4	2.0	1.5	0.18	0.14
9.99	−14.0	−12.9	2.6	2.4	0.26	0.24
10.59	−13.0	−13.3	2.3	2.3	0.24	0.25
12.39	+21.2	+20.2	3.2	3.0	0.39	0.37

TABLE 5.

a- and b-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H_2)
1.25	+8.7	12.1	0.15
1.99	−1.1	1.0	0.02
2.99	−10.2	6.0	0.18
3.97	−0.8	0.4	0.01
4.99	+2.1	0.8	0.04
5.95	+4.8	1.4	0.09
7.03	+9.2	2.3	0.16

Table 5.—(*Continued*)

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H_2)
7.93	−10.1	2.2	0.18
8.91	−9.5	1.9	0.17
10.05	−12.2	2.2	0.22
10.77	−13.1	2.2	0.23
11.97	+25.8	3.8	0.46.

Part of the expenses of this study is defrayed with the Research Fund of the University, for which we desire to tender our gratefulness.

Summary.

As we have performed various kinds of experiments with the stick antimony electrode, changing their conditions of electrodes and external influences, we may summarise the results of our observations.

(1) The stick antimony electrode in an unstirred solution in contact with air at equilibrium gives a reliable measurement of pH values from pH 1 to 9 inclusive. Recognizing some decrease of accuracy in the results, we may of course apply this electrode for the determination of pH values above pH 9, up to 12.

(2) The value of E.M.F. (m.v.) with the electrode prepared by a Japanese sample and measured against the saturated calomel electrode is obtained by the equation $E = 53.8 \text{ pH} - 0.7$.

(3) We did not take the temperature as a calculating factor, but we always record it during our observation, and we know that E.M.F. value becomes invariably greater when the temperature rises. All our experiments have been made with a temperature varying between 10°C. and 25°C., and the mean error due to the temperature gradient, in this case, is, on an average, about 4%, which is comparable to other experimental errors easily inserted in the estimation of the hydrogen ion concentration.

(4) The surface of a polished antimony electrode is probably covered in a solution with an oxide whose colour is dependent on the pH value of the solution, and the change is more striking when the solution is more acidic. When the pH value of the solution is 1 to 8, the surface of the electrode immersed in the solution becomes black, but if the

solution is alkaline (pH is 9 to 12), the immersed part shows a whitish shade of colouring.

(5) When pH is small, i.e. acidic, we generally obtain a higher value of E.M.F. at the beginning of the experiment, and the value decreases and tends to a point of equilibrium; but the opposite takes place in the case of an alkaline solution whose pH is great. We may think that colour change on the surface of the electrode immersed in a solution has perhaps some relation to this transformation of the direction of E.M.F.

(6) The time to reach equilibrium is also dependent on the pH value of the solution. It is comparatively short when the solution is slightly alkaline and its pH value is about 8 to 9, and the colour on the surface of the electrode due to the immersion cannot easily be found in this range of pH. But when the solution is strongly acidic (small pH) or strongly alkaline (large pH), the surface of the electrode changes readily in colour, and the time to reach equilibrium becomes longer.

(7) As for the effect of stirring a solution, E.M.F. deviates to a higher side after it has once reached equilibrium. If we stir the solution from the beginning of the experiment (continuous stirring), E.M.F. thus obtained gives generally a higher value than it is unstirred but when we stop the vibration, E.M.F. value decreases.

(8) Mechanical treatment by the preparation of the stick antimony electrode (Ex. emery paper for polishing) is rather little influenced for obtaining the E.M.F. value, but the original minute impurities contained in an electrode, and the porousness of the electrode cannot be neglected in the determination of E.M.F.

(9) When we have once observed with a solution saturated with antimony oxide, results are obtained at equilibrium, and they are nearly similar to those of an ordinary case. We may, therefore, conclude that the chemical change of the electrode, often discussed by some authors, is not a great factor in the use of the antimony electrode.

(10) When we immersed two electrodes in the same solution but, at different times, the course followed to reach equilibrium are nearly parallel. If the equilibrium is once established by an electrode in a given solution, and we only change the electrode with a polished one, or use the same after polished it again, nearly the same course taken in the first case may also be followed to obtain an equilibrium value.

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