

[CONTRIBUTION FROM THE POND CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

THE STICK ANTIMONY ELECTRODE: PREPARATION AND CALIBRATION¹

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RECEIVED AUGUST 3, 1931

PUBLISHED MARCH 5, 1932

Introduction

The stick antimony electrode has been recognized as being a practical and useful method for electrometric titrations and the measurement of hydrogen-ion concentration of solutions which cannot be determined by either the hydrogen or the quinhydrone electrodes, notably colloids and dyestuffs. It is much sturdier than the glass electrode and calibration before each measurement is not essential.

When a metal is in equilibrium with its oxide, which is slightly soluble in solution, an electrode potential is set up which is a measurement of the hydrogen-ion concentration of that solution.² The electrode used in this investigation was a cleaned and polished metallic stick. The antimony trioxide is present as an adsorbed film on the metal. This film is formed easily and rapidly in dry air.³ The presence of moisture aids in the formation of this film.⁴ Kolthoff and Hartong, Roberts and Fenwick⁵ and Britton and Robinson⁶ added antimony trioxide to the solution to be measured. Franke and Willaman⁷ and Snyder⁸ were among the first to use the stick antimony metal as an electrode without the use of the added oxide.

Uhl and Kestranek⁹ kept the solution in motion by passing in washed air. This procedure of keeping the liquid in motion has been carried on by other investigators using different methods. Kolthoff and Hartong state that an inert gas, as nitrogen or hydrogen, may be used. However, mechanical stirring has been employed by the majority of investigators. Franke and Willaman prefer "stirring without unnecessary agitation" while Britton and Robinson state that vigorous stirring gives best results.

¹ This paper is a portion of a thesis offered by H. C. Beard in partial fulfillment of the requirements for the M. S. degree in the School of Chemistry and Physics at the Pennsylvania State College.

² Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

³ Tammann, *ibid.*, [4] **4**, 546 (1923).

⁴ Ditte and Metzner, *Compt. rend.*, **115**, 938 (1892); Thiele, *Ann.*, **263**, 361 (1891); Ruff and Albert, *Ber.*, **38**, 54 (1908); Milbauer and Slemr, *Chem. Listy*, **20**, 392 (1926); Clarke, *Analyst*, **54**, 99 (1929); Grant, *ibid.*, **54**, 227 (1929).

⁵ Roberts and Fenwick, *THIS JOURNAL*, **50**, 2125 (1928).

⁶ Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

⁷ Franke and Willaman, *Ind. Eng. Chem.*, **20**, 87 (1928).

⁸ Snyder, *Soil Science*, **26**, 107 (1928).

⁹ Uhl and Kestranek, *Monatsh.*, **44**, 29 (1923).

Brewer and Montillon¹⁰ bubbled nitrogen through a closed electrode vessel while Snyder used a closed mechanical shaking electrode system. Unstirred solutions were used in this investigation.

Cast electrodes were prepared as suggested by Franke and Willaman. Attempts were made to increase the oxide film but the electrodes gave best results when polished clean with emery cloth and rinsed with distilled water. Using the simple potentiometric method with these electrodes it was impossible to get a stable point of equilibrium due to drifting of the potential. This drifting seemed to be almost a definite variable, which was probably due to polarization of the electrode. Drifting was greatest in the acid and alkaline ranges and least in the neutral range.

In order to overcome any possible effects due to polarization, a vacuum-tube potentiometer, such as is used with glass electrodes, was constructed. Since the function of a vacuum-tube potentiometer is to cut down to a minimum the flow of current to the electrode, polarization is also reduced to a minimum. By using this system, antimony electrodes in an unstirred buffer solution gave a stable reproducible equilibrium point very quickly.

It is the purpose of this investigation to show that, with the use of the vacuum-tube potentiometer, stick antimony electrodes in unstirred solution in contact with air may be calibrated against buffer solutions of different P_{H} values to give a curve which agrees with that of the hydrogen electrode as to slope, thus satisfying the Nernst equation, from the P_{H} value of 2 to that of 7. Advantages of this system, due to the prevention of polarization, are noted and the effect of the stirring or the bubbling of a gas through the solution is discussed.

Experimental Apparatus and Procedure

The electrodes were cast from Mallinckrodt's c. p. and Baker's c. p. analyzed antimony in glass tubes of 6 mm. bore. In some cases the electrodes were cooled very slowly in a temperature controlled furnace and in other cases they were allowed to cool normally to the temperature of the room. With the slow cooling sticks large crystals of the metal were obtained and with the rapid cooling fine crystals, as was noted by Bekier.¹¹ Electrical connections were made to the antimony electrode by soldering on a piece of copper wire to one end of the stick. The electrodes varied in length from 6 to 13 cm. In use they were immersed in the buffer solution to a depth of about 4 cm. They were always polished bright and clean with fine emery cloth and rinsed with distilled water just before using. Eight different electrodes were used and compared in the course of the investigation.

The buffer solutions used were Clark and Lubs' standard mixtures, Sørensen's standard glycol mixtures, and Ringer's mixtures.¹² All of these buffer solutions were checked with a hydrogen electrode.

The apparatus used in the determinations was the standard Hydrogen-Ion Po-

¹⁰ Brewer and Montillon, *Trans. Am. Electrochem. Soc.*, **55**, 356 (1929).

¹¹ Bekier, *Z. anorg. Chem.*, **78**, 178 (1912).

¹² Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1928, 3d ed.

tentiometer Outfit of Leeds and Northrup using the saturated calomel cell. The standard cell was checked against one calibrated by the Bureau of Standards. Several calomel cells were carefully made and frequently checked against each other. The mercury was purified by the method of Hulett.¹³ The vacuum-tube potentiometer is of a design developed by E. A. Lantz of the Hercules Powder Company.

All measurements were taken at a temperature of 25°.

Experimental Data

A. With the Use of the Potentiometer.—Readings were taken with the potentiometer and the vacuum-tube potentiometer separately for the purpose of comparison. With the potentiometer alone, in acid, neutral and alkaline buffer solutions, there was considerable instability of the point of equilibrium. In some cases a peak was obtained and in others not. Readings were taken at minute intervals.

The drifting is not very great but it is a question of just what is the correct value. Comparative readings with buffer solutions of different *PH* values may be taken at the end of a specified time but it is no criterion as to the accuracy of the results.

These same solutions were also measured using the vacuum-tube potentiometer for comparison as noted in Table I.

TABLE I
COMPARISON OF RESULTS WITH THE POTENTIOMETER AND THE VACUUM-TUBE POTENTIOMETER

<i>P_H</i>	Vacuum-tube potentiometer v.	Potentiometer (5 min. rdgs.). v.	Difference, mv.
2.32	0.1297	0.1287	1.0
4.97	.2861	.2848	1.3
7.67	.4469	.4462	0.7
10.70	.6048	.5972	7.6

It is noticeable that the difference is slight in the *P_H* range of 2 to 8 but of considerably greater value in the alkaline range. These results would seem to justify the use of the potentiometer only in the former range to get acceptable values for general purposes.

B. Readings with the Vacuum-tube Potentiometer.—Readings made with the vacuum-tube potentiometer were very constant. The equilibrium point was obtained only in the time it took to balance the apparatus, which was rarely over a minute. The accuracy of the instrument is about 2 mv. and this would be the only deviation from the equilibrium point in prolonged readings. Readings were taken to tenths of a millivolt so that a more accurate average of all of the different electrodes would be obtained. There was no evidence of any drifting, except possibly in the high alkaline range where the electrode no longer gives a true measurement of the hydrogen-ion concentration.

¹³ Hulett, *Phys. Rev.*, **21**, 388 (1905).

There was no attempt made to use either the electrodes or the buffer solutions in any particular order, as advised by Roberts and Fenwick. The readings were taken over a period of several weeks and are brought together in Table II. The readings in all cases are definite equilibrium points obtained and not averages.

It is notable that all of these electrodes, made at different times under different conditions, should give such concordant results. The greatest deviation of any electrode from the average is 3.5 mv. except in the high alkaline range. It will be noticed that in the high alkaline and acid ranges there seems to be a grouping of the electrodes, A, B and D giving high readings while the other group gives lower. Upon examination of the electrodes it was found that those of the former group were of large crystalline structure while those of the latter were made up of fine crystals. This is in agreement with Getman,¹⁴ who found that cadmium electrodes of a large crystal give higher potential readings than those of a fine polycrystal structure.

TABLE II

THE MEASURED E. M. F. OF THE CELL $\text{Sb} \mid \text{Sb}_2\text{O}_3, \text{ SOLUTION} \parallel \text{SATD. KCl, Hg}_2\text{Cl}_2 \mid \text{Hg}$
WITH DIFFERENT STICK ANTIMONY ELECTRODES

PH	Electrodes								Av. v.	Max. dev. from av., mv.
	A v.	B v.	C v.	D v.	K v.	M v.	N v.	O v.		
1.30	0.0768	0.0800	0.0822	0.0817	0.0777	0.0760	0.0768	0.0777	0.0786	3.6
1.60	.0912	.0896	.0898	.0896	.0896	.0889	.0938	.0938	.0908	3.0
2.24	.1250	.1290	.1290	.1250	.1250	.1250	.1250	.1290	.1265	1.5
2.98	.1689	.1711	.1712	.1700	.1680	.1681	.1690	.1691	.1694	1.8
3.98	.2275	.2297	.2284	.2279	.2259	.2295	.2266	.2283	.2280	2.1
4.97	.2868	.2884	.2876	.2839	.2839	.2868	.2870	.2847	.2861	2.3
7.00	.4076	.4077	.4082	.4032	.4077	.4030	.4046	.4060	.4060	3.0
7.87	.4592	.4532	.4568	.4581	.4535	.4570	.4522	.4552	.4557	3.5
8.81	.5003	.5003	.4976	.4997	.5008	.5010	.5008	.4985	.4999	2.3
9.81	.5541	.5510	.5519	.5509	.5508	.5518	.5510	.5510	.5516	2.5
10.53	.5939	.5947	.5938	.5948	.5938	.5947	.5939	.5930	.5941	1.1
11.29	.6588	.6548	.6506	.6580	.6553	.6506	.6482	.6530	.6537	5.5
11.86	.7283	.7344	.7213	.7283	.7223	.7215	.7189	.7210	.7240	10.4
12.01	.7678	.7774	.7608	.7736	.7570	.7608	.7509	.7618	.7638	13.6

Since an equilibrium point was reached so nicely with an unstirred solution, experiments were performed to find the effect of stirring the solution and also the bubbling of so-called inert gases.

These experiments showed that stirring lowers the potential and the amount of change is proportional to the rate of stirring. Stirring affects the solution in at least two ways. It increases the concentration of potassium chloride in the solution by causing currents to flow past the saturated potassium chloride junction of the calomel electrode. Stirring also naturally increases the amount of air, and thus of oxygen, in the solu-

¹⁴ Getman, *J. Phys. Chem.*, **35**, 588 (1931).

tion. Harrison and Vridhachalam¹⁵ and Snyder also note that the potentials obtained in unstirred solutions are somewhat higher than those in stirred solutions. Procopiu¹⁶ states that the movement of an electrolyte with reference to a metal electrode causes an electromotive force.

It was found, by experimentation, that bubbling a gas through the buffer solution, when in contact with the stick antimony electrode, made a considerable difference in the potential obtained. Nitrogen, hydrogen, oxygen and air were bubbled through fresh buffer solutions. With all of these gases equilibrium points were obtained by the use of the vacuum-tube potentiometer within a few minutes. There is little doubt that in these cases a gas-metal electrode has been formed. French and Kahlenberg¹⁷ state that with a gas-metal electrode the "total combination potential is due both to absorbed gas and to a condensed film of gas on the surface of the metal." The potential "depends on the gas dissolved in the electrolyte and not that in the gas phase." They also state that oxygen tends to make the metal potentials less basic, while nitrogen and hydrogen have the opposite effect. This was found to be the case with these gases in use with the antimony electrode. Bubbling of a gas and stirring tend to prevent the formation of a film of gas about the electrode and so a lower potential results than when the solution is at rest, saturated with the dissolved gas.

Discussion

The value of the potential developed in an oxidation-reduction reaction is calculated by the Nernst equation

$$E = E_0 - \frac{RT}{nF} \ln C$$

The value of E_0 is a constant depending on the electrode system. The potential of any electrode system which functions to measure hydrogen-ion concentration may be determined by the Nernst equation

$$E = E_0 - \frac{RT}{F} \ln (H^+)$$

This being the case, any change in E represents a change in the hydrogen-ion concentration. As the equation

$$E = E_0 - \frac{RT}{F} \ln (H^+) = E_0 - 2.3 \frac{RT}{F} \log (H^+)$$

and since the term $2.3 RT/F$ at 25° has the value of 0.05915, noted by Lewis and Randall¹⁸ and $P_H = -\log (H^+)$, the equation $E = E_0 + 0.05915 P_H$ is obtained.

¹⁵ Harrison and Vridhachalam, *Mem. Dept. Agr. India, Chem. Ser.*, **10**, 157 (1929).

¹⁶ Procopiu, *Z. physik. Chem.*, **A154**, 322 (1931).

¹⁷ French and Kahlenberg, *Trans. Am. Electrochem. Soc.*, **54**, 163 (1928).

¹⁸ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

When E is plotted against P_H and E_0 is a constant, the slope of the line should be 0.05915. As shown in Fig. 1 this holds true for the stick antimony electrode in unstirred solutions in contact with air between the P_H values 2.2 to 7.8. The line for this electrode passing through these points intercepts the abscissa at the value of -0.007 v. Below the P_H value of 2.2 and above the P_H of 7.8 the stick antimony electrode does not function to measure correctly hydrogen-ion concentration.

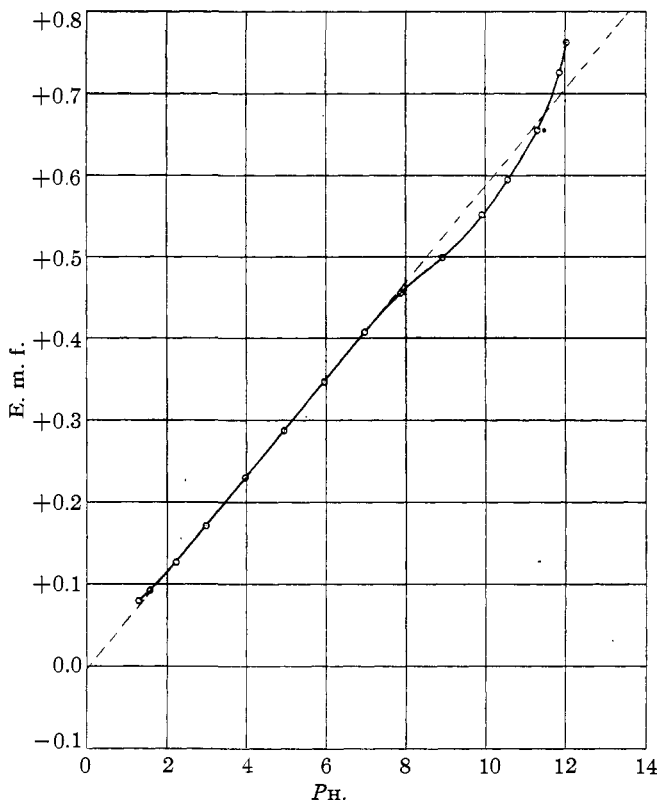


Fig. 1.—Calibration curve for the stick antimony electrode.

In Table III the value of E_0 is calculated from the observed value of E . Since $E_0 = E + 0.05915 P_H$, the value of E_0 may be calculated from the equation $E_0 = E - 0.05915 P_H$, using the P_H values obtained with the hydrogen electrode. Since E is the value obtained with the saturated calomel electrode, E_0 is the potential of the stick antimony electrode referred to the saturated calomel electrode.

The average value of E_0 from P_H 1.60 to 7.87 of the cell $\text{Sb} | \text{Sb}_2\text{O}_3, \text{Solution} || \text{satd. KCl, Hg}_2\text{Cl}_2 | \text{Hg}$ is -0.0070 v. The average of the E_0 values from P_H 2.24 to 7.00 is -0.0071 v. The value taken for the calculation of

TABLE III
 E_0 AND P_H VALUES WITH THE STICK ANTIMONY ELECTRODE

P_H (Table I)	E (obsd), v.	E'' (0.05915 P_H), v.	E_0 ($E - E''$), v.	P_H (Sb/Sb ₂ O ₃), calcd.	P_H Diff. (Sb to H ₂)
1.30	0.0786	0.0769	+0.0017	1.45	+0.15
1.60	.0908	.0946	- .0038	1.65	+ .05
2.24	.1265	.1325	- .0060	2.26	+ .02
2.98	.1694	.1763	- .0069	2.98	.00
3.98	.2280	.2354	- .0074	3.97	- .01
4.97	.2861	.2940	- .0079	4.96	- .01
5.96	.3459	.3525	- .0066	5.97	- .01
7.00	.4060	.4141	- .0081	6.98	- .02
7.87	.4557	.4655	- .0098	7.82	- .05
8.81	.4999	.5211	- .0212	8.57	- .24
9.81	.5516	.5803	- .0287	9.44	- .37
10.53	.5941	.6228	- .0287	10.16	- .37
11.29	.6537	.6678	- .0141	11.17	- .12
11.86	.7240	.7015	+ .0225	12.36	+ .50
12.01	.7638	.7104	+ .0534	13.03	+1.02

the P_H of the antimony electrode is -0.007 v. Thus the Nernst equation for this electrode at 25° in this range of P_H values is $E = -0.007 + 0.05915 P_H$ when the antimony electrode is measured against a saturated calomel electrode, considering E to be positive when the saturated calomel electrode is positive.

Since the normal calomel electrode referred to the hydrogen electrode is 0.037 v. more positive than the saturated calomel electrode to the same reference,¹⁹ the Nernst equation referring to the normal calomel electrode becomes $E' = + 0.030 + 0.05915 P_H$, considering E' positive when the normal calomel is positive.

The value of E_0 as calculated with the saturated calomel electrode agrees well with the intercept of the curve with abscissa as shown in Fig. 1. It will be noticed that the greatest deviation of the antimony electrode from the hydrogen electrode between the P_H values of 2.2 and 7.0, inclusive, is $\pm 0.02 P_H$, and between the P_H values of 1.6 and 7.8 is $\pm 0.05 P_H$.

Upon examination of the curve of Fig. 1 it will be noticed that the nature of the curve varies with different degrees of P_H . It is only where the curve is straight and of the proper slope (from P_H 2 to 7) that it gives a true measurement of the hydrogen-ion concentration.

Comparison of Results with those of Other Investigators of Antimony Electrodes.—There have been a number of investigators who have worked with antimony-antimony oxide electrodes. The electrodes have

¹⁹ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore Md., 1928, 3d ed.

been of three types: the metallic stick, the plated and the dropping electrode of Roberts and Fenwick. Shukov and Aveyevich²⁰ and Brinkman and Buytendiyk²¹ used electrodes made by plating out antimony metal on a platinum electrode. All of the other investigators previously mentioned in this article used the stick metal electrode. This type of electrode has been favored because of its ease of preparation and applicability. A comparison of the results, as noted by the Nernst equation, arrived at by different investigators proves interesting. The potential of the antimony electrode against the normal calomel electrode is taken as the basis.

TABLE IV
COMPARISON OF RESULTS OF INVESTIGATORS WITH THE Sb | Sb₂O₃ ELECTRODE

	Stick metal electrode
Franke and Willaman	$E = 0.050 + 0.054 P_H$
Lava and Hemedes ²²	$E = 0.052 + 0.057 P_H$
Kolthoff and Hartong	$E = 0.0415 + 0.0485 P_H$ (P_H 1-5) 14°
	$E = 0.009 + 0.0536 P_H$ (above P_H 9) 14°
Britton and Robinson	$E = 0.018 + 0.0534 P_H$ (calcd. from curve)
Harrison and Vridhachalam	$E = 0.0234 + 0.0498 P_H$ 30°
This investigation	$E = 0.030 + 0.05915 P_H$
	Plated electrode
Shukov and Aveyevich	$E = 0.009 + 0.053 P_H$
	Dropping electrode
Roberts and Fenwick	$E = 0.138 + 0.05915 P_H$

With the stick metal electrodes all of the solutions were stirred with the exception of those of Harrison and Vridhachalam and the present investigation. It will be noted that in no case, with the stirred solutions, is the slope of the curve the correct theoretical value. The comparison of the E_0 value of Harrison and Vridhachalam and this investigation is noteworthy as both were obtained with unstirred solutions. The difference in temperature and the drawing of a line to meet all possible points in their investigation might account for the difference in the slope of their curve.

The difference in the E_0 value between the present investigation and that of Roberts and Fenwick may be explained by the difference in the nature of the electrode. They used a dropping electrode and were very careful to exclude all air in their closed electrode vessel, replacing it with nitrogen. Our electrode vessel was open to the air and the solution contained the normal amount of dissolved air at atmospheric conditions. Our experiments showed that the addition of more air to the solution lowers the potential, so it is reasonable to believe that a system with the air and

²⁰ Shukov and Aveyevich, *Z. Elektrochem.*, **35**, 349 (1929).

²¹ Brinkman and Buytendiyk, *Biochem. Z.*, **199**, 387 (1928).

²² Lava and Hemedes, *Philippine Agr.*, **17**, 337 (1928).

oxygen excluded, as that of Roberts and Fenwick, will give higher potentials.

Summary

1. The use of a vacuum-tube potentiometer with stick antimony electrodes eliminates drifting of the potential and gives rapid, constant and reproducible readings.

2. Stirring of a solution or the bubbling of a gas through it causes a deviation of the values away from the theoretical.

3. The stick antimony electrode in an unstirred solution in contact with air at equilibrium with both antimony and antimony trioxide gives a correct measurement of P_H values from P_H 2 to 7 inclusive. The value of E with this electrode measured against the normal calomel electrode is obtained by the equation $E = +0.030 + 0.5915 P_H$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

PHOTOMETRIC DETERMINATION OF THE SOLUBILITY OF SILVER CHLORIDE AND OF MERCUROUS CHLORIDE¹

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RECEIVED AUGUST 25, 1931

PUBLISHED MARCH 5, 1932

Introduction

Utilization of the Tyndall beam in the determination of the amount of suspended material in dispersed systems has often been attempted. As pointed out by Wells,³ the phenomena encountered are extremely complex. Turbidity is doubtless a measure of other factors beside concentration. In spite of such limitations, methods employing the Tyndall beam possess certain attractive features, one of the most significant of which is that of extreme sensitivity.

Nephelometric analysis, employing the comparison of intensity of light reflected by a suspension of unknown concentration with that from a suspension of the same substance of known concentration, is a convenient method for the quantitative estimation of a solid phase in suspension. It is unsuited to the precise determination of solubility because of the necessity for the presence of a definite quantity of the solid phase in the standard.

Popoff and Neuman⁴ appear to have been the first to utilize an optical method involving the estimation of the solubility of a sparingly soluble inorganic salt by noting the first appearance of the Tyndall beam in a

¹ For suggestion of the problem and for generous assistance in the earlier part of the work the authors are indebted to the late Stephen Popoff.

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³ P. V. Wells, *Chem. Reviews*, **3**, 331-382 (1927).

⁴ Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853-1860 (1930).