STUDIES IN ANTIMONY ELECTRODE.

By D. N. Mehta and S. K. Kulkarni Jatkar.

In spite of the large number of papers on the use of antimony electrode for pH measurements, there is considerable difference of opinion about the method of preparing the electrode, the constants of the electrode system and the range of pH over which it is supposed to work; and very few could discuss their results from the theoretical point of view owing no doubt to the erratic and unsatisfactory nature of this electrode for accurate work. This electrode has mostly been used for electrometric titrations.

The problem arose in this laboratory in connection with the determination of pH of clays, tannins and basic lead salts where the hydrogen electrode could not work and the results obtained with the quinhydrone electrode needed checking with another electrode.

The theory of the antimony electrode is as follows. The potential between antimony and a liquid depends upon the concentration of the ions that the electrode can deliver. In the case of trivalent antimony electrode we have

$$E_{sb} = E'_0 - RT/3F \log_e (Sb^{\cdot\cdot\cdot})$$

where $E'_0 = RT/nF \log_e (P/Sb^{\cdot\cdot\cdot})$ and P being the Nernst solution pressure, and since the term $2{\cdot}3\ RT/F$ has the value of 0·05915, at 25°C.,

$$E_{sb} = E'_0 - \frac{0{\cdot}05915}{3} \log (Sb^{\cdot\cdot\cdot}) \quad .. \quad .. \quad (1)$$

If we take an oxide of antimony which has a very little solubility product, the metal ion concentration is governed by the hydrogen ion concentration as follows:—

$$Sb_2O_3(s) + 3\,H_2O \rightleftharpoons 2\,Sb^{\cdot\cdot\cdot} + 6\,(OH)^-$$

$$\therefore (Sb^{\cdot\cdot\cdot})^2 \times (OH')^6 = Ks$$

$$\therefore Sb^{\cdot\cdot\cdot} = \frac{\sqrt{Ks}}{(OH')^3}.$$

Now $H^{\cdot} \times OH' = Kw$.

substituting the value for (OH'), we have

$$Sb^{\cdot\cdot\cdot} = \frac{\sqrt{Ks} \times (H^{\cdot})^3}{(Kw)^3}$$

wherefore, substituting in equation (1) the value for the activity of $Sb^{\cdot\cdot\cdot}$, we have

$$
\begin{aligned}
E_{sb} &= E'_0 - \frac{0\cdot05915}{3} \log \left\{ \frac{Ks^{\frac{1}{2}} \times (H^{\cdot})^3}{(Kw)^3} \right\} \\
&= E'_0 - \frac{0\cdot05915}{3} \{\log (Ks)^{\frac{1}{2}} + \log (\dot{H})^3 - \log (Kw)^3\} \\
&= E'_0 - 0\cdot05915 \{\log (Ks)^{1/6} + \log (\dot{H}) - \log (Kw)\} \\
&= E'_0 + 0\cdot05915 \{-\log (Ks)^{1/6} - \log (\dot{H}) + \log (Kw)\} \\
&= E'_0 + 0\cdot05915 \{pH - 1/6 \log (Ks) + \log (Kw)\}
\end{aligned}
$$

$$\therefore E_{sb} \text{ at } 25°C = E_0 + 0\cdot05915 \, pH. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where E_0 the E.M.F. of an oxide electrode against the hydrogen electrode is given by the E.M.F. of the cell PtH_2 | solution of any pH ‖ Sb_2O_3 | Sb, the electrode reaction being

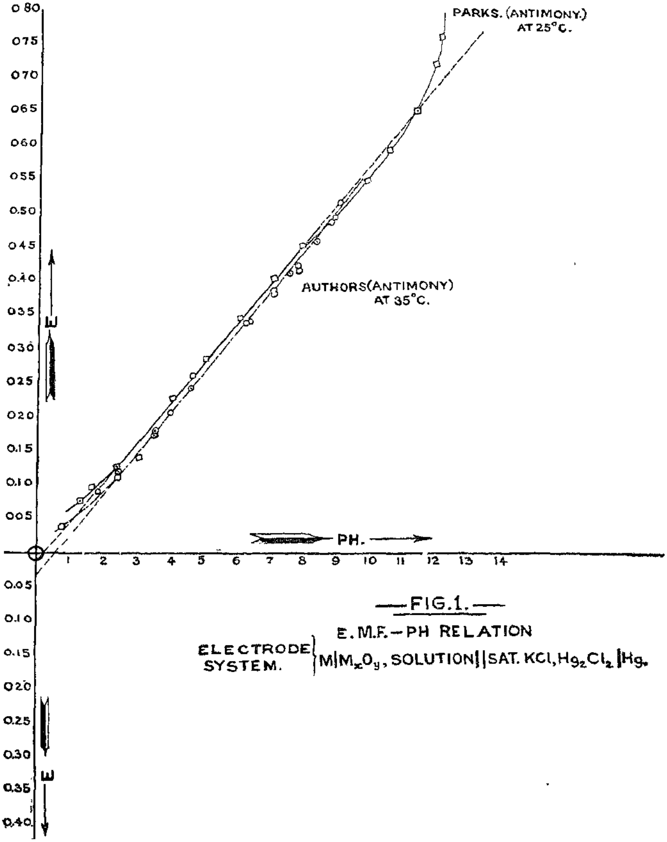
$$Sb_2O_3 \times 6H \rightleftharpoons 2\, Sb^{\cdot\cdot\cdot} + 3H_2O.$$

From (2) it follows that the value of the electrode potential varies linearly with the hydrogen ion concentration, the slope at 25° being 0.05915. The range of pH over which the linear relationship holds is governed by the solubility of the oxide in solutions of different pH, an amphoteric oxide with small solubility product being indicated.

Most of the workers have used the antimony electrode after allowing an oxide film to form by dipping the metal in various solutions for a long time and added antimony trioxide to the solution in order to saturate the solution with the oxide and obtained varying and incorrect values for the slope of the pH against electromotive force. The following Table I summarises some of the more important papers on the subject.

Roberts and Fenwick (*Loc. cit.*) obtained the theoretical value for the slope by using the system antimony in the form of crystal and antimony oxide in definite cubic form, and they also checked the value of E_0 independently. Unfortunately they did not measure the temperature coefficient of their electrode system and compare the heat values deduced with the thermo-chemical data.

The other work which has yielded the correct slope is that of Parks and Beard obtained for polished antimony electrode using valve potentiometer. In the recent work, Ball, Schmidt and Bergstresser (*Loc. cit.*) report a theoretical slope at 20°, working under exactly the same conditions as those of Parks and Beard. But the values of E_0 of these authors differ among themselves and considerably so from that of Roberts and Fenwick, pointing to the existence of oxides other than antimony trioxide or mixtures of different oxides. It is interesting to note that, except the work of Roberts and Fenwick who definitely used Sb_2O_3, all the work including ours which has yielded correct slope is with polished electrode made from cast antimony. Therefore, cast antimony metal must be containing sufficient oxide to give stable electromotive force. This surprising fact was already noted in the



—FIG.1.—

E.M.F.—PH RELATION

ELECTRODE SYSTEM. $M|M_xO_y$, SOLUTION||SAT. KCl,Hg_2Cl_2|Hg.

early work by Uhl and Kestranek (*Monatsh,* 1923, 44, 29) and also more recently by Britton and Robinson (*Loc. cit.*). No one, however, has so far attempted to investigate the nature of this oxide. We have shown in this paper that the oxide is antimony tetroxide on thermodynamical grounds. We have also analysed previous data by applying the theoretical slope and our experimentally determined temperature coefficients and have shown that the previous values for polished cast antimony lie on either side of those of ours as shown in the last column

TABLE I.

Authors	Nature of the electrode	Temp. oC	Empirical formula	Range of pH	E_0 at 25°
Franke and Willaman[1]	Cast in air.	25	0·050 +0·054 pH	1–12	0·257av. 1-8 pH.
Lava and Hemedes[2] ..	Cast in air with white and yellow oxide.	26–29	0·052 +0·057 pH	2–8	0·255av. 0·030 2–5 pH. 0·344 10 ,,
Kolthoff and Hartong[3] ..	Stick—Sb_2O_3 in N_2.	14 14	0·0415+0·0485 pH 0·009 +0·0536 pH	1–5 8–12	
Harrison and Vridhachalam[4]	Tarnished electrode.	30	0·0234+0·0498 pH	4-8	0·326 9 pH. 0·300av. 4–8 ,,
Tetuo Tomiyama[5] ..	,,	20	0·022 +0·0567 pH	..	.. ..
King[6]	,,	24	0·019 +0·0575 pH	3–12	.. ..
Shukov and Aveyevich[7]	Plated electrode.	14	0·009 +0·053 pH	3–9	0·290av. 3–8 pH.
Roberts and Fenwick[8] ..	Dropping electrode.	25	0·138 $+\underline{0{\cdot}05915}$ pH	1–10	0·1445 1–10
Britton and Robinson[9] ..	Bright stick.	14	0·018 +0·0534 pH	1–11	0·240 2–6 pH. 0·270 9 ,, 0·276 10 ,,
Parks and Beard[10] ..	Polished stick.	25	0·030 $+\underline{0{\cdot}05915}$ pH	2–7	0·254 2–7 pH. 0·276 10 ,,
T. R. Ball, Webster, B., Schmidt and Karl S., Bergstresser[11]	,,	20	0·017 $+\underline{0{\cdot}05813}$ pH	2–7	0·288 ,,
Authors	,,	25	0·0077 $+\underline{0{\cdot}0591}$ pH	2–8	0·276 2·4–8·4 pH

[1] *Ind. Eng. Chem.*, 1928, **20**, 87.

[2] *Philippine Agr.*, 1928, **17**, 337.

[3] *Rec. trav. chim. Pays-Bas*, 1925, **44**, 113

[4] *Mem. Dept. Agr. India*, 1929, **10**, 157.

[5] *J. Biochem. Japan*, 1933, **18**, 285; *American Chem Abst.*, 1934, **28**, 701

[6] *Jour. Ind. Eng. Chem. Anal. Ed*, 1933, **5**, 323.

[7] *Z. Elektrochem*, 1929, **35**, 349–352: 1931, **37**, 771.

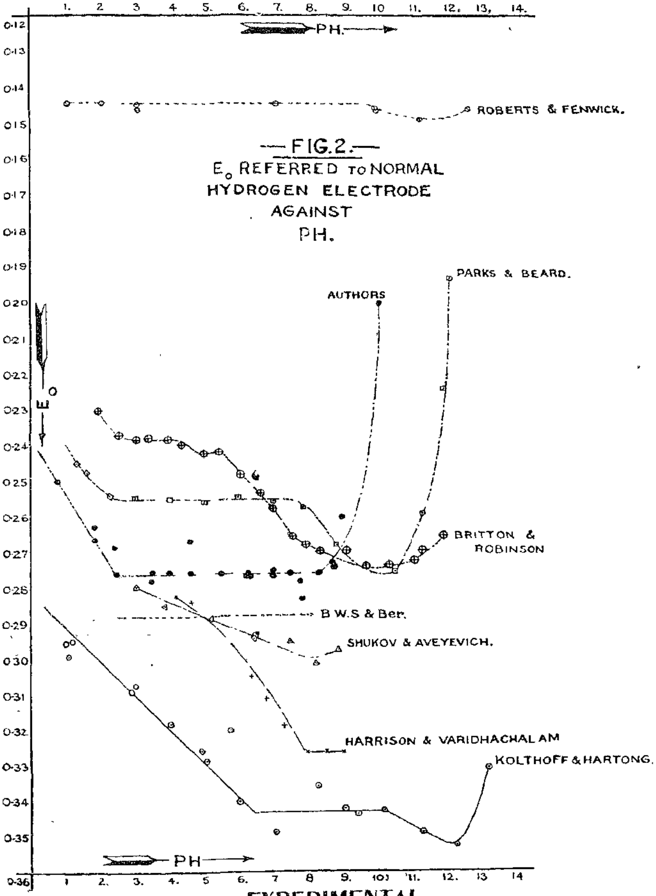
[8] *J. Amer. Chem. Soc.*, 1928, **50**, 2125.

[9] *J. Chem. Soc.*, 1931, 458.

[10] *J. Amer. Chem. Soc.*, 1932, **54**, 856.

[11] *Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 60

of Table I and in Fig. 2, the discrepancies being attributed to existence of small quantities of other oxides depending upon the method of cooling.



—FIG. 2.—

E_0 REFERRED TO NORMAL HYDROGEN ELECTRODE AGAINST PH.

EXPERIMENTAL.

The electrode used was Kahlbaum's pure antimony used for atomic weight determinations. The electrode was about 40 mm. in length, and in use was immersed in the buffer solutions to a depth of about 20 mm. It was always polished bright and cleaned with fine emery paper (grade 00) and rinsed with distilled water just before using.

Antimony trioxide used was purified and freed from traces of antimony pentoxide and iron impurities according to Schuhmann's method (*J. Amer. Chem. Soc.*, 1924, **46**, 52). The buffer solutions used were Clark and Lub's standard mixtures, all of these having been checked either against the quinhydrone or the hydrogen electrodes.

A saturated calomel cell was used as a reference electrode. The mercury used was distilled and highly purified. Potassium chloride and ammonium nitrate solutions were used as junction liquids.

All measurements were carried out in an oil bath kept at about 25° C. (Fig. 3). The vacuum tube potentiometer described by us in a previous paper was used (*Proc. Ind. Acad. Sci.*, 1934, **1**, 390).

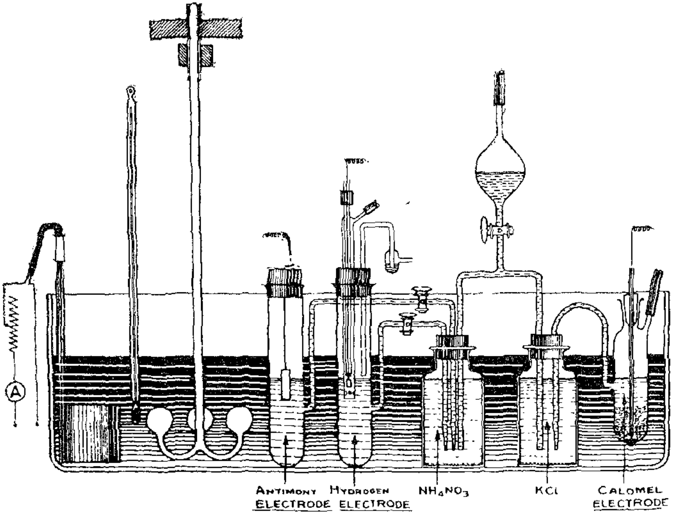


FIG. ③ APPARATUS FOR MEASURING PH OF SOLUTIONS.

Readings obtained with the vacuum tube potentiometer were very stable. The equilibrium point was obtained very quickly. First reading recorded was taken 15 minutes after the electrode was set up. Readings were estimated to a tenth of a millivolt. The drifting was not very great, the maximum variation being three units in the fourth place in about a quarter of an hour after the equilibrium had been reached. In highly alkaline solutions there was a drift of about three millivolts in about the same time. In this range, the electrode does not function to measure true hydrogen ion concentration.

An experiment was conducted to determine if the added oxide as distinct from the oxide formed as film on the surface of the electrode, takes any part in the electrode reaction. The results did not show any difference; the experiment was carried out in a solution of pH 5. (*cf.* This Journal Vol. **18A**, Part XI, p. 82.)

The values of E_0 and E are shown in Tables II (*a*) and II (*b*). These have been deduced from the observed results as shown in Tables III (*a*) and III (*b*) by applying the temperature correction of variation of the potential of saturated calomel cell (column 7) and for that of E_0, *viz.*, 3.3 millivolt per degree, (column 6) found later.

TABLE II (*a*).

pH	E_0 in volt	E at 25°C deduced from the formula $E=E_0+0\cdot05915$ pH
1·797	−0·0166	0·0897 volt
2·421	−0·0296	0·1135 ,,
3·446	−0·0313	0·1724 ,,
4·591	−0·0202	0·2512 ,,
6·230	−0·0295	0·3388 ,,
6·284	−0·0302	0·3413 ,,
6·953	−0·0292	0·3819 ,,
7·466	−0·0291	0·4123 ,,
7·767	−0·0366	0·4226 ,,

TABLE II (*b*).

0·7436	−0·0034	0·0405 volt
1·855	−0·0198	0·0898 „
2·395	−0·0217	0·1199 „
3·476	−0·0289	0·1766 „
4·011	−0·0292	0·2079 „
4·595	−0·0286	0·2430 „
5·448	−0·0294	0·2925 „
6·245	−0·0292	0·3400 „
6·995	−0·0284	0·3851 „
7·491	−0·0283	0·4136 „
7·527	−0·0295	0·4157 „
7·720	−0·0313	0·4250 „
8·290	−0·0292	0·4609 „
8·764	−0·0274	0·4907 „
8·758	−0·0261	0·4916 „
8·970	−0·0136	0·5167 „

DISCUSSION OF RESULTS.

In Tables II (*a*) and II (*b*) last column, E.M.F.'s observed have been calculated for exactly 25°C., and have been plotted against pH values as shown in Fig. 1. Since E_0 is a constant quantity, the slope of the line should be 0.0591. This relation holds good for the antimony electrode between pH value of 2.4 to that of 8.4. The line passing through points 2.4 and 8.4 intercepts the abscissa at the value of −0.0293 volt.

In Tables III (*a*) and III (*b*), the values of E_0 have been calculated from the observed values of E, using the pH values obtained either with quinhydrone or with the hydrogen electrodes. The values of E_0 are the potentials of the stick antimony electrode at various hydrogen ion concentrations referred to a saturated calomel electrode at 25°C.

TABLE III (*a*).

Temp. C.	Quinhydrone E. M. F. observed in volt	pH	Antimony E. M. F. observed in volt	E_0 in volt	E_0 corrected for temperature		E_0 in volt with reference to normal hydrogen electrode
					Sb	Calomel	
25·94°	0·3455	1·80	0·0936	–0·0130	–0·0161	–0·0166	–0·2633
25·04°	0·3092	2·42	0·1136	–0·0295	–0·0296	–0·0296	–0·2763
25·03°	0·2486	3·45	0·1725	–0·0312	–0·0313	–0·0313	–0·2780
25·00°	0·1810	4·59	0·2511	–0·0202	–0·0202	–0·0202	–0·2669
24·77°	0·0845	6·23	0·3375	–0·0304	–0·0296	–0·0295	–0·2762
25·29°	0·0803	6·28	0·3429	–0·0290	–0·0300	–0·0302	–0·2767
25·00°	0·0412	6·95	0·3819	–0·0292	–0·0292	–0·0292	–0·2759
24·71°	0·0104	7·47	0·4117	–0·0303	–0·0293	–0·0291	–0·2760
25·24°	0·0066	7·77	0·4231	–0·0357	–0·0365	–0·0366	–0·2833

The average value of E_0 from pH 2.4 to pH 8.4 of the cell $Sb/Sb_2O_3,|solution||sat.KCl|Hg_2Cl_2|Hg$ is −0.0293 volt. E_0 in the lower range up to pH 2.4 increased rapidly with the increasing value of pH, then remained constant, irrespective of pH, up to 8.4 pH, and then in the alkaline range E_0 decreased with the corresponding increase in the pH. On noticing this behaviour of E_0 in varying its value with different degrees of pH, it was thought worthwhile to recalculate the values of E_0 from the readings of the previous workers by giving the correct slope for the pH–E.M.F. relation at the observed temperature and reducing the values of E_0 to 25° by applying the temperature coefficient observed by the authors. These are shown in Fig. 2.

Harrison and Vridhachalam's (*Loc. cit.*) values showed quite a different behaviour of E_0 from that of the authors. The value of E_0, increased with the increasing pH, reached a maximum (.326) at 8 pH and was constant up to 9 pH. The results of Shukov and Aveyevich (*Loc. cit.*), who used a plated electrode, showed a similar behaviour, the average value of E_0 being .30 volt.

The values of E_0 calculated from the results of Kolthoff and Hartong showed a similar behaviour; the curve reached a maximum (about .345 volt) at about 7 pH, remained constant up to 11 pH and then again decreased with the increasing pH. In this case, antimony electrode was agitated by means of an inert gas.

TABLE III (*b*).

Temp. C.	Quinhydrone E. M. F. observed in volt	pH	Antimony E. M. F. observed in volt	E_0 in volt	E_0 corrected for temperature		E_0 in volt with reference to normal hydrogen electrode
					Sb	Calomel	
23·90°	0·4087	0·74	0·0434	−0·0004	−0·0040	−0·0034	−0·2501
25·57°	0·3424	1·86	0·0922	−0·0176	−0·0195	−0·0198	−0·2665
25·00°	0·3107	2·40	0·1199	−0·0217	−0·0217	−0·0217	−0·2684
25·33°	0·2466	3·48	0·1781	−0·0276	−0·0287	−0·0289	−0·2756
25·50°	0·2147	4·01	0·2103	−0·0272	−0·0289	−0·0292	−0·2759
25·30°	0·1804	4·60	0·2445	−0·0274	−0·0284	−0·0286	−0·2753
25·49°	0·1297	5·45	0·2950	−0·0275	−0·0291	−0·0294	−0·2761
25·21°	0·0826	6·25	0·3412	−0·0284	−0·0291	−0·0292	−0·2759
25·30°	0·0384	7·00	0·3867	−0·0272	−0·0282	−0·0284	−0·2751
25·50°	0·0086	7·49	0·4163	−0·0273	−0·0290	−0·0293	−0·2760
25·50°	0·6920H	7·53	0·4181	−0·0275	−0·0292	−0·0295	−0·2762
25·13°	0·0042Q	7·72	0·4257	−0·0308	−0·0312	−0·0313	−0·2780
26·20°	0·7381H	8·29	0·4675	−0·0246	−0·0286	−0·0292	−0·2759
25·00°	0·7648H	8·76	0·4907	−0·0274	−0·0274	−0·0274	−0·2741
25·27°	0·7653H	8·76	0·4936	−0·0251	−0·0260	−0·0261	−0·2728
25·50°	0·7775H	8·97	0·5195	−0·0116	−0·0133	−0·0136	−0·2603

The values obtained by Roberts and Fenwick were quite constant up to 10 pH, then reached the maximum and again showed a tendency to decrease with increasing pH. The latter behaviour is shown by most of the curves drawn. They used a dropping electrode with cubic form of Sb_2O_3 and were careful to replace air by nitrogen in the electrode vessel.

Parks and Beard's values of E_0, when plotted against pH show a very close similarity with that of the authors' curve. Their value of E_0 also increased rapidly with the increasing pH up to 2.4 and then were constant up to 7.5 pH. In the alkaline range, the values of E_0 obtained by Parks and Beard increased with the increasing value of pH, reached a maximum which is the same as the authors' value in the lower range, and then again began to decrease with the corresponding increase in pH. The absolute value of E_0 obtained by Parks and Beard was lower than ours by 22 millivolts.

The extra liquid junction of ammonium nitrate used in our experiments is responsible for a maximum difference of .5 millivolt in the value of E_0 obtained by the authors and that of Parks and Beard found under the same conditions in other details.

The discrepancies in the values of E_0 found by various workers for polished electrodes are also likely to be due to part of the antimony existing in allotropic form. We intend to settle this point by using a single crystal of stable form of antimony.

Since E_0 at 25°C. for a metal|metal oxide electrode is essentially the potential of the electrode in a solution containing hydrogen ions at unit activity referred to hydrogen electrode in a similar solution, the value of E_0 was determined directly. For this purpose an H form of the cell shown in Fig. 4 was used. The measured E.M.F. of the cell $Pt,H_2|solution,||Sb_xO_y|Sb$ at 25°C. and 685 mm. pressure is as follows:—

pH	E. M. F. observed	Time
6·026	0·2774 volt	8·30 A.M.
	0·2774 „	8·50 A.M.
	0·2775 „	9·20 A.M.
	0·2773 „	9·45 A.M.

The above results compare favourably with the value of E_0 obtained indirectly by using the equation $E = E_0 + 0.05915\,pH$, which is $(0.0293 + 0.2467) = -0.2760$. Most of the discrepancy of 1.4 millivolts is due to the two junction potentials. Therefore, the mean value of E_0 is taken as 0.2767 volt when referred to the normal hydrogen electrode and –0.0293 volt when referred to a saturated calomel electrode at 25°.

Ball, Schmidt and Bergstresser (*Loc. cit.*) found the value of E_0 different from that obtained by Parks and Beard. The value of E_0 obtained by them is –0.020 volt at 20°, although these investigators carried out their experiments under the same conditions as those of Parks and Beard. The difference was due to the high temperature coefficient of the antimony electrode as found in the experiments described in the next paragraph. The value of E_0 calculated for 25°C. by applying the temperature coefficient comes to −.288, our value lying intermediate between this and that obtained by Parks and Beard.

The experiments were carried out to measure the temperature coefficient of the antimony electrode. The E.M.F.'s of the cell Pt,H_2|solution,||Sb_xO_y|Sb at two different temperatures were noted. The H form of the cell in Fig. 4 was transferred from the large bath kept at 25° to the Dewar flask kept at 40°C.

pH	E. M. F. observed	Time	
6·026	0·2774 volt	8·30 A.M.	25°C.
	0·2774 ,,	8·50 A.M.	
	0·2775 ,,	9·20 A.M.	
	0·2773 ,,	9·45 A.M.	
6·026	0·2279 volt	9·55 A.M.	40°C.
	0·2278 ,,	10·15 A.M.	
	0·2278 ,,	10·45 A.M.	
	0·2280 ,,	11·10 A.M.	

From the above results, the value of the temperature coefficient for the antimony electrode equals −0.0033 volt per degree. The value obtained by Von G. P. Awsejwitsch and J. J. Shukoff (*Loc. cit.*) was 0.00025 volt per degree for the range 15–30°. The electrode used by these authors was prepared by plating on platinum a bright deposit of antimony by electrolysis of $SbCl_3$ solutions of acetonitrile or formic acids.

Still more recently, Tetuo Tomiyama (*J. Biochem. Japan,* 1933, **18**, 285; *American Chem. Abst.,* 1934, **28**, 701) using an electrode prepared by dipping it for several days in alkali obtained temperature coefficients which varied from 1.5 to 3 millivolts per degree in the range 10–30° for solutions 2 to 11 pH. His formula E = .022 + .0567 pH at 20° (using calomel electrode) shows that the wrong slope he obtained is due to the oxide being not at unit concentration as required theoretically.

The following Table IV shows the values of free energy and heat content calculated from the value of E_0 obtained by Roberts and Fenwick (*Loc. cit.*), Parks and Beard (*Loc. cit.*) and the authors for the formation of various possible oxides from elements.

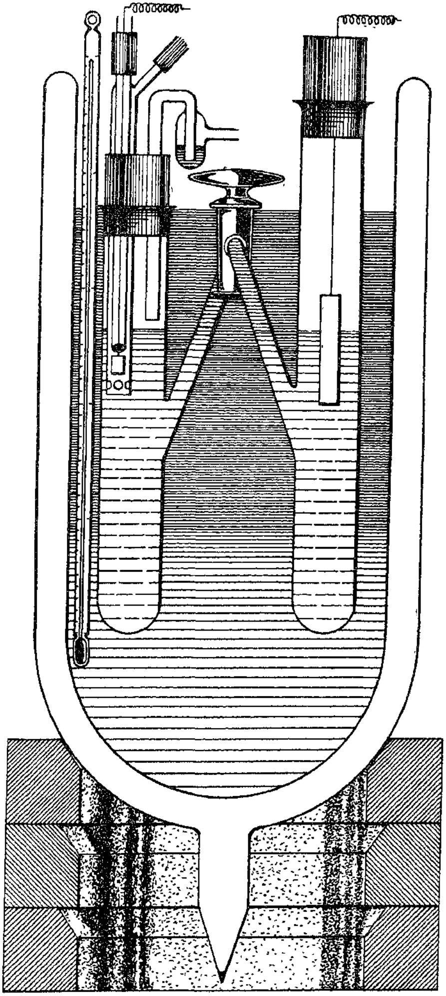


FIG. 4.

CELL. Pt, H_2 | SOL^{N} Sb_xO_y | Sb.

TABLE IV.

Electrode system	Free energy A=nFE			Heat of reaction	
	Roberts and Fenwick	Parks and Beard	Authors	Calculated	Observed[1]
Sb_2O?		44790	43820	49320	....
Sb_2O_3	149670	134380	131470		167400
Sb_2O_4		179170	175300	*197290*	*195290*
Sb_2O_5		223950	219120	246600	210325

The last column gives the value for the heat content calculated by assuming that the free energy was constant for the small range 25° to 40° in the integration of Gibbs Helmholtz equation

$$A - Q = T\frac{dA}{dT}, \quad nFE - Q = nFT\cdot\frac{dE}{dT} \quad \text{and} \quad \frac{\delta F}{T_1} - \frac{\delta F}{T_2} = Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

It will be noticed that the heat of reaction so calculated somewhat agrees with that observed by Simon and Thaler for antimony tetroxide. Mixter (*Amer. J. Sci.*, 1909, **28**, 109) gives 209800 as the value for the same oxide obtained thermochemically. The approximate nature of the agreement is as much due to small temperature range over which E.M.F.'s were measured as the uncertainty in the thermochemical data itself.

The possibility of existence of Sb_2O_4 in the cast antimony electrode is not a surprise in view of the fact that this is the only oxide stable in the range of the melting point of antimony which must be dissolving sufficient quantity of the oxide at the high temperature of casting to function in the polished electrode. Experiments are under way to settle this point by measuring the potential of $Sb|Sb_2O_4$ electrode.

The question of possible formation of suboxide Sb_2O is not, however, excluded as the corresponding study of bismuth electrode shown elsewhere gives energy calculations in agreement with the existence of Bi_2O and the greyish black film observed in the case of antimony may as well be Sb_2O which was reported by Berzelius to form when antimony was exposed to moist air and by F. Jones (*J. Chem. Soc.*, 1876, **29**, 641) who obtained it by the action of stibine on alkaline lye.

It was often observed by the authors that a very thick film of oxide formed on the surface of the metal prevented its functioning

---

[1] Simon and Thaler, *Zeit. anorg. Chem.*, 1927, **162**, 253.

as an electrode. The coating of the film of oxide in course of time grew thick. The electrode was then scraped with the fine emery cloth, polished and washed with distilled water before use, when it again began to function as a metal-oxide electrode. This observation clearly supports the view that the electrode reaction takes place at the surface of the metal and is not affected if only a very thin film of the oxide is formed on it. The erratic nature of the results when a thick film is formed may be in some way connected with the electrolytic valve action of this metal found by Gunther-Sulze.

It was also noted that the film of oxide coated on the surface of the metal was greyish black in colour, when the stick was immersed in solution of pH values up to 8. The interesting point about the film of oxide observed was the change in colour it underwent from greyish black to white, when immersed in the solution of pH values of more than 8. A similar observation was also recorded by Taku Uemura and Hideo Sueda (*Bull. Chem. Soc. Japan*, 1933, 8, 1).

SUMMARY AND CONCLUSION.

1. Attempt has been made to interpret the accumulated empirical data for the polished antimony electrode in order to know the reaction in the cell Pt,H_2|solution of any pH||Sb_xO_y|Sb, (for different oxides of antimony).

$$Sb_xO_y + H \rightleftharpoons Sb + H_2O.$$

2. It has been shown that the formation of films obtained by dipping the electrode for long time results in the incorrect value of the slope of pH-E.M.F. relation, probably due to the activity of the oxide forming the film, changing with pH.

3. The best results were obtained with freshly-polished cast electrodes which come to equilibrium within a quarter of an hour and could be used for all the measurements during the day. Thus reproducible values with theoretical slope were ensured. The relation between the pH and the E.M.F. is expressed by $E = -0.0293 + 0.0591$ pH at 25° when measured against saturated calomel electrode in the range 2.5 to 8.5 pH with an accuracy of 0.01 pH.

4. The value of E_o has been confirmed by direct determination of the E.M.F. of the system

Pt.H_2|solution of any pH||Sb_xO_y|Sb at 25° = 0.277 volt.

The temperature coefficient of the above has been determined to be 3.3 millivolts per degree.

The somewhat small capacity and larger temperature coefficient of the electrode system makes the use of an oil thermostat and the valve electrometer essential for accurate work especially in the alkaline range

5. The value of the heat of reaction calculated by Gibbs Helmholtz equation indicates the existence of the tetroxide of antimony in the sample used.

Our thanks are due to Dr. H. E. Watson for his interest during the progress of this work.

Department of General Chemistry,
Indian Institute of Science,
Bangalore.

[Received, 11-5-1935.]

853-35.—Printed at The Bangalore Press, Bangalore City, by T. Subramania Aiyar, Superintendent.