STUDY OF THE BISMUTH ELECTRODE.

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This paper describes the results of experiments carried out with the bismuth electrode under conditions similar to those used in our study of the antimony electrode (*cf.* This *Journal*, **18A**, pp. 85–100), with a view to find out its suitability for measuring pH. Incidentally the results throw light on the nature of the oxide which is responsible for the interference colours on the metal.

The electrode was a piece of metal 30 mm. long, selected from pure crystalline bismuth supplied by Merck. It was never polished with emery cloth and, when not in use, was always kept immersed in distilled water. The metal remained quite bright throughout the measurements unlike the antimony which rapidly tarnished. No bismuth oxide was used, as it was concluded from the experiments with antimony electrode that the electrode reaction was dependent on the thickness and stability of the film of oxide on the surface of the metal. The buffer solutions were Clark and Lub's standard mixtures, all of these having been checked either against the quinhydrone or hydrogen electrode. A saturated calomel cell was used as a reference electrode. Only one liquid junction was used in this case. The measurements were carried out at about 30°C., the vacuum tube potentiometer previously described being used. The values of E_o and E calculated from the equation $E = E_o + .06011$ pH (30°C.) are shown in Table I. These have been deduced from the observed results as shown in Table II, by applying the temperature correction of variation of the potential of the saturated calomel (column 7), and for that of E_o, *viz.*, 1.5 millivolts per degree (column 6), found later.

Since E_o is a constant quantity, the slope of the line should be 0.06011. This relation holds good for the bismuth electrode between pH values of 5.0 and 7.4. Beyond the limits of 5.0–7.4, although the electrode ceases to function as a theoretical electrode, the linearity relation holds good and the hydrogen ion concentration can be measured by the help of a calibration curve.

TABLE I.

pH	E_0 in volt	E at 30°C.
1·796	—0·0966	0·0114 volt
2·739	—0·1274	0·0372 „
3·823	—0·2165	0·0133 „
4·253	—0·2141	0·0416 „
4·867	—0·2149	0·0776 „
	—0·2217	0·1405 „
	—0·2198	0·1424 „
6·026	—0·2111	0·1511 „
6·533	—0·2285	0·1642 „
7·313	—0·2240	0·2156 „
7·752	—0·2337	0·2328 „
8·056	—0·2488	0·2355 „
8·610	—0·2051	0·2525 „
9·095	—0·2700	0·2768 „
9·194	—0·2703	0·2824 „
2·739	—0·1345	0·0301 „

TABLE II.

Temp. C.	Quinhydrone E. M. F. observed in volt	pH	bismuth 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
					Bi	Calomel	
29·52°	0·3440	1·80	0·0103	—0·0975	—0·0968	—0·0966	—0·3403
29·95°	0·2869	2·74	0·0372	—0·1275	—0·1274	—0·1274	—0·3711
29·50°			0·0278	—0·1356	—0·1348	—0·1345	—0·3782
29·00°	0·2227	3·82	0·0106	—0·2185	—0·2170	—0·2165	—0·4602
29·20°	0·1968	4·25	0·0393	—0·2157	—0·2145	—0·2141	—0·4578
30·30°	0·1587	4·87	0·0787	—0·2142	—0·2147	—0·2149	—0·4586
30·93°			0·1436	—0·2198	—0·2212	—0·2217	—0·4648
30·22°			0·1430	—0·2194	—0·2197	—0·2198	—0·4635
30·26°	0·0901	6·03	0·1519	—0·2106	—0·2110	—0·2111	—0·4548
30·28°	0·0583	6·53	0·1652	—0·2280	—0·2284	—0·2285	—0·4722
30·05°	0·0120	7·31	0·2157	—0·2239	—0·2240	—0·2240	—0·4677
30·86°	0·0151	7·75	0·2345	—0·2220	—0·2333	—0·2337	—0·4774
30·20°	0·7283H	8·06	0·2363	—0·2484	—0·2487	—0·2488	—0·4925
30·72°	0·7621H	8·610	0·2552	—0·2636	—0·2647	—0·2651	—0·5088
29·93°	0·7904H	9·10	0·2766	—0·2701	—0·2700	—0·2700	—0·5137
30·46°	0·7970H	9·19	0·2841	—0·2694	—0·2701	—0·2703	—0·5140

In Table II, the values of E_0 have been calculated from the observed values of E, using the pH values obtained either with the quinhydrone or with the hydrogen electrodes. The values of E_0 are the potentials of crystalline bismuth electrode at various hydrogen ion concentrations referred to a saturated calomel electrode at 30°C. The average values of E_0 from pH 5.0–7.4 for the cell

Bi|Bi oxide|solution||sat. KCl.|Hg_2Cl_2|Hg

is $-0.2231 \pm .007$ volt.

As in the case of antimony, the temperature coefficient of bismuth electrode was measured. The E.M.F.'s of the cell

$Pt.H_2|solution||Bi\ oxide|Bi$

at two different temperatures were measured and are given as under :—

TABLE III.

pH	E. M. F. observed	Time
6·026	0·4737 volt	11·30 A.M.
	0·4737 „	11·50 A.M.
	0·4738 „	12·10 P.M.
	0·4737 „	12·30 P.M.

E_0 at 30°C. is —0·4737 volt.

The above value of E_0 agrees with the value deduced from the slope of the graph of E *vs.* pH within the experimental error. The correct value of E_0 is taken as equal to −0.4737 volt with respect to normal hydrogen electrode and −0.2300 volt with respect to saturated calomel electrode at 30°C.

TABLE IV.

pH	E. M. F. observed	Time
6·026	0·4592 volt	12·40 P.M.
	0·4591 „	1·0 P.M.
	0·4592 „	1·20 P.M.

E_0 at 40°C. is —0·4592 volt.

From the above results we notice that the temperature coefficient for the electrode system in the case of bismuth|bismuth oxide is −0.0015 volt per degree.

The following values of free energy and heat content were calculated from the observed E.M.F. at two different temperatures and are compared with thermochemical data for the possible oxides of bismuth.

TABLE V.

Electrode system	Free energy A=nFE	Heat of reaction	
		Calculated	Observed
Bi | Bi_2O	35000	*67800*	*66270* (1)
Bi | Bi_2O_3	105000	203400	137800 (2)
Bi | Bi_2O_4	140000	271200	
Bi | Bi_2O_5	175000	349000	

(1) This value has been calculated from the value of heat of solution of Bi_2O in hydrochloric acid obtained by Tanatar (*Zeit. anorg. Chem.*, 1901, **27**, 437)

$$3\ Bi_2O+6\ HCl=2\ BiCl_3+3\ H_2O+4\ Bi+25412 \text{ calories}$$

and that given by Metzner (*Comptes Rendus*, 1892, **115**, 1303) for

$$2\ Bi+3\ O+6\ HCl=2\ BiCl_3+3\ H_2O+224200 \text{ calories}.$$

(2) Mixter (*Amer. Jour. Sci.*, 1909, **28**, 109).

The results point to the existence of bismuth suboxide in the surface film.

SUMMARY AND CONCLUSION.

Experiments with bismuth electrode with interference colours on the surface due to the oxide film revealed only a short range over which it can be used to measure pH. The energy calculations agree with the electrode system Bi|Bi_2O.

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