

362. *Potential-pH Dependence of the Bismuth Electrode in and out of Contact with Air.*

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The static potential of the bismuth electrode in buffers over almost the whole pH range was investigated. With unprotected electrodes from different sources the potential-pH relation was not a simple linear function over the whole range, and, though consistent with one another, the results could not be readily interpreted in terms of those computed thermodynamically for the presence of any one definite oxide. With protected electrodes, prepared by distilling the hydrogen-reduced metal out of contact with air, the behaviour at pH 11.5—13.0 was in accordance with that of the Bi-Bi₂O₃ system, and at pH 9.0—10.5 with that of the Bi-BiO·OH system. At pH 4.0—8.0 an equilibrium involving the metal and BiO⁺ ions through BiO and BiO·OH as intermediates was assumed to determine the electrodic equilibrium. In the most acid buffers containing chloride ions, and in hydrochloric acid solutions of various concentrations from pH 0.8 to pH 2.8, the behaviour was in accordance with that of the Bi-BiOCl system.

LITTLE is known of the equilibrium (or equilibria) which determines the variation of the static potential of the bismuth electrode with pH. Mehta and Kulkarni,¹ from measurements with massive electrodes over the pH range 5.0—7.4 at 30°, inferred that the suboxide Bi₂O governed the functioning of the electrode as a metal-metal oxide electrode. For the constant e_0 , *viz.*, potential at unit hydrogen-ion activity, and the coefficient $\partial e/\partial \text{pH}$ they reported the values 0.4737 v on the normal hydrogen scale and 0.060 v/pH unit respectively. From measurements with various forms of bismuth electrode Schwabe² inferred that the potential was a simple linear function of pH from 3 to 14, the corresponding constants being respectively 0.391 v and 0.0507 v/pH unit at 20°. Schwabe and Philipp concluded that the response of the electrode to pH could be explained on the assumption of the existence of Bi(OH)₃ on the metal surface.³ Similar conclusions were reached by Kriventsova and Shatalov,⁴ who inferred that in neutral and slightly alkaline solutions the potential was determined by an equilibrium involving the metal and the trioxide while in strongly alkaline ones the metal behaved as a mixture of an oxide and an oxygen electrode.

Previous work on the arsenic and antimony electrodes^{5,6} showed that in air they behaved as if governed by an "oxygen overvoltage effect and were legitimately called metal-metal oxide-oxygen electrodes *". From protected electrodes freed previously from the air-formed film such an effect was absent, and the behaviour accorded with that expected from an equilibrium involving the metal and the trioxide.

* *I.e.*, the difference between the potential in air and that computed thermodynamically for one stoichiometric oxide as found to occur in absence of oxygen.

¹ Mehta and Kulkarni, *J. Indian Inst. Sci.*, 1935, **18**, A, 109.

² Schwabe, *Z. Elektrochem.*, 1949, **53**, 125.

³ Schwabe and Philipp, *ibid.*, 1951, **55**, 411.

⁴ Kriventsova and Shatalov, *Zhur. fiz. Khim.*, 1953, **27**, 1476.

⁵ Tourky and Moussa, *J.*, 1948, 752, 756.

⁶ *Idem*, *J.*, 1949, 1297, 1302.

We have now re-examined the behaviour of the bismuth electrode on open circuit in and out of contact with air to discover the extent to which the results can be reconciled with previous ones.

EXPERIMENTAL

Electrodes.—For measurements in air massive and electrodeposited bismuth were used. The first type were of the following qualities: (1) specially prepared bismuth, (2) bismuth from B.D.H., (3) bismuth from Hopkin and Williams, and (4) a Heliger spectrally pure brand; all in the form of cylindrical rods which were carefully abraded with 3/0 emery paper then rubbed against cotton wool. The pure metal was prepared as suggested by Schneider and Mylius⁷ by starting with C.P. (chemically pure) bismuth nitrate. Bismuth was electrodeposited (5) on

FIG. 1. Apparatus for preparation of oxide-free electrodes.

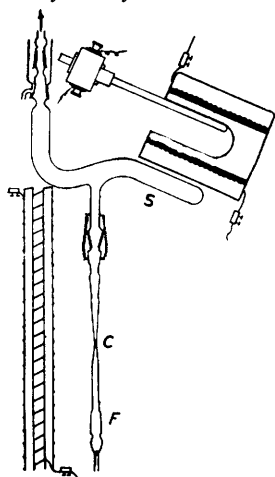
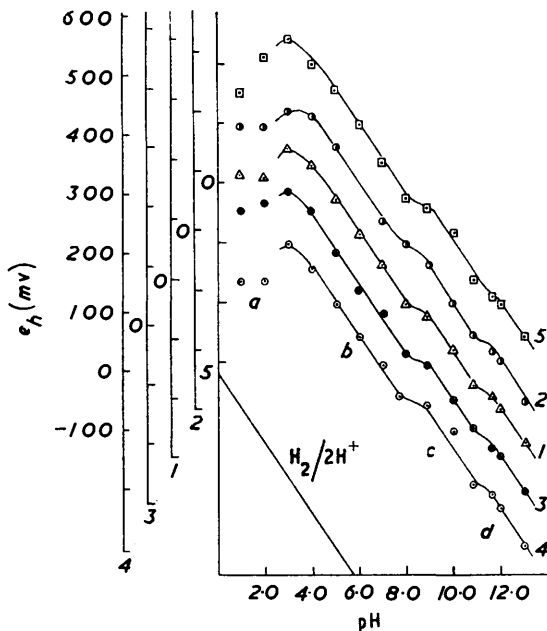


FIG. 2. Potential-pH curves for unprotected electrodes.



For key, see text.

copper-coated platinum by the method of Vozdvizhenskii *et al.*,⁸ a fresh deposit being used in each measurement.

Oxide- and oxygen-free bismuth for electrodes was prepared by distilling the hydrogen-reduced metal out of contact with air, the device shown in Fig. 1 being used. About 3 g. of the pure metal were heated under purified hydrogen at 600–650° in the silica portion S connected to a vacuum line. After four cycles of heating in hydrogen for ½ hr. followed by evacuation, the temperature was raised to 1000–1200°, whereupon the metal started to distil. The fine glittering droplets were received in the electrode jacket F which was surrounded with an electric oven at 300°. The distilled metal spread over a very short platinum wire at the bottom of the jacket which served then to maintain electrical contact. Distillation was continued until almost all the metal was transferred (if much was left, the silica tube often cracked on cooling). After thorough evacuation the electrode jacket was sealed at the fine constriction C. This was then broken under oxygen-free solution in a cell similar to that described before.⁶

Solutions.—For pH 1–10 Clark and Lubs's series of buffer mixtures was used.⁹ Buffer

⁷ Archibald, "Preparation of Pure Inorganic Compounds," Wiley, New York, 1932, p. 276.

⁸ Vozdvizhenskii *et al.*, *Trans. Butlerov Inst. Chem. Tech., Kazan*, 1934, No. 1, 102.

⁹ See Clark, "Determination of Hydrogen Ions," Baillere, Tindall, and Cox, London, 3rd edn., 1928, p. 200.

of pH 10.4 was selected from Kolthoff's series, and for the most alkaline buffers Ringer's mixtures were used; ¹⁰ 0.2M-sodium hydroxide solution, pH 13.0, completed the series. Hydrochloric acid solutions were obtained by appropriate dilution of a constant-boiling mixture. All pH values were checked against a hydrogen electrode.

Measurements.—These were all carried out at $25^\circ \pm 0.1^\circ$ in an air-bath, and potentials were recorded on an ordinary potentiometer against a saturated calomel half-cell; precautions were taken to avoid the diffusion of chloride ions into the test solution. The potential values cited, however, are on the normal hydrogen scale.

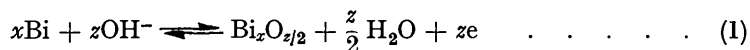
RESULTS AND DISCUSSION

With unprotected electrodes in solutions not freed from dissolved oxygen the static potential recorded 30 min. after immersion remained practically constant during up to 3 hr. This was particularly so in the most alkaline buffers where the maximum difference did not exceed 5 mv. In buffers of pH 4—8, and in the most acid ones containing chloride ions, the change in potential over that period amounted on average to 10 and 15 mv. respectively. On the basis of the final potentials recorded, the plots shown in Fig. 2 were obtained. In no case can the relation be considered a simple linear one over the whole pH range. Except for portion (a), corresponding to the most acid buffers, each curve consists of three portions (b), (c), and (d) possessing nearly the theoretical slope and extending respectively over the approximate pH ranges 4.0—8.0, 9.0—10.5, and 11.5—13.0. The e_0 values (volts) computed for the different portions were as follows:

Electrode	Portion (b)	(c)	(d)
(1) Prepared	+0.426	+0.466	+0.492
(2) B.D.H.	0.432	0.468	0.488
(3) Hopkin and Williams	0.418	0.462	0.486
(4) Spectroscopic	0.420	0.466	0.486
(5) Electrodeposited	0.448	0.490	0.510

Except for the electrodeposited metal, which always gave somewhat more positive potentials, the agreement between the results for the various other electrodes may be considered highly satisfactory, so there seems little doubt that the relatively low values of both slope and e_0 reported by Schwabe ² are both due to the assumption that a simple linear relationship holds over the pH range 3—14. The e_0 value within portion (b) is, on average, some centivolts lower than that, 0.474v, reported by Mehta and Kulkarni ¹ for the approximate pH range 5—7; their value approaches that for portion (c).

The free energies of formation of the oxides BiO, Bi₂O₃, and Bi₂O₄ as calculated by Latimer ¹¹ are respectively -43.2, -116, and -109 kcal./mole. From these values, and a metal—metal oxide electrode equilibrium such as (1) being assumed, the corresponding e_0 values are 0.292 v, 0.386 v and 0.638 v respectively. The experimental



values are higher than that computed for the Bi-BiO system and all of them lie between those for the Bi-Bi₂O₃ and the Bi-Bi₂O₄ system, so the behaviour of the unprotected electrode cannot be explained simply by assuming that one definite stoichiometric oxide exists on the surface and governs its functioning as a metal—metal oxide electrode. No free-energy data have been reported for the suboxide Bi₂O, but our results with the protected electrode make it unnecessary to consider that this oxide governs the electrode equilibrium (1).

With the protected electrode, prepared by distillation and examined in oxygen-free solutions, the static potentials showed remarkable constancy. During 24 hr., or sometimes 48 hr., the maximum change did not exceed 2—3 mv. The potential-pH curve

¹⁰ Britton, "Hydrogen Ions," Chapman and Hall, London, Vol. I, 1942, p. 311.

¹¹ See Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1938, p. 115.

for such an electrode (Fig. 3) shows the same general features as those for the unprotected electrodes; the corresponding portions (a), (b), (c), and (d), as well as the transitional pH ranges connecting them are, however, better defined. The curve is shifted bodily towards less positive potentials, e_0 corresponding to portions (b), (c), and (d) being 0.335 v, 0.366 v, and 0.389 v respectively. The last value agrees satisfactorily with that computed for the Bi-Bi₂O₃ system (0.386 v), which indicates that at pH 11.5–13.0 the trioxide, or the ortho-base Bi(OH)₃, is the stable phase in contact with the metal; the hydration energy can be neglected, as shown by Latimer.¹¹ However, the transformation of the ortho-base to the meta-base BiO·OH is apparently associated with appreciable change in free energy, as can be seen as follows: The solubility of BiO·OH in water was reported by Almkvist¹² to be 5.8×10^{-6} mole/l. The value obtained in this laboratory during a study of the amphoteric properties of bismuth oxides was found, however, to be only 2.8×10^{-6} mole/l.

FIG. 3. Potential-pH curves for protected electrodes.

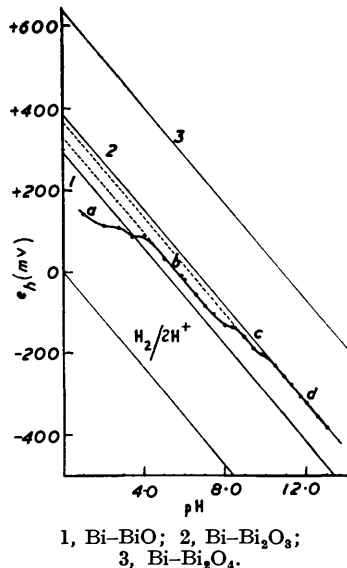
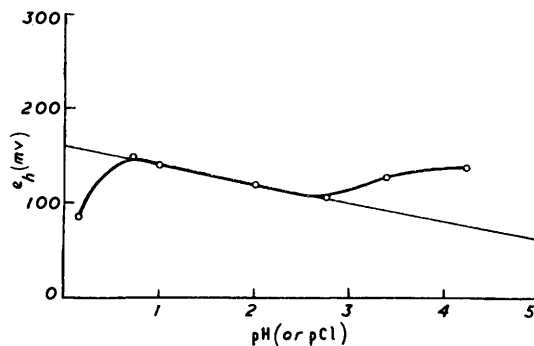


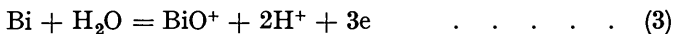
FIG. 4. Potential-pH curves for a protected electrode in solutions of hydrochloric acid.



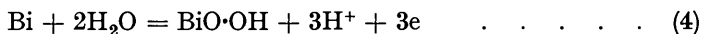
Using our value and assuming complete dissociation into BiO⁺ and OH⁻ ions, we find that the free-energy change for the equilibrium (2), as calculated from $\Delta F = -RT \ln K$,



where K is the solubility product, is 15,150 cal./mole. From this value and taking ΔF° for BiO⁺ to be -34,960 cal./mole, as computed from the standard potential value 0.314 v for the half-reaction (3) reported by Smith¹³ from direct cell measurements, we find ΔF° for BiO·OH to be -87,700 cal./mole; the values of ΔF° used for OH⁻ and H₂O were those



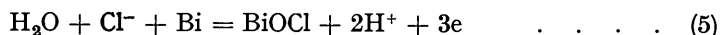
quoted by Latimer.¹¹ From the derived free-energy values, e_0 for the half-reaction (4)



was calculated as 0.369 v, agreeing with that found experimentally to hold within portion (c), and thus indicating that the meta-base is the most stable phase in contact with the metal at pH 9.0–10.5.

¹² Almkvist, *Z. anorg. Chem.*, 1908, **103**, 240.
¹³ Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 360.

Before commenting on the e_0 value for portion (b) for the protected electrode, we consider measurements with this electrode in hydrochloric acid solutions of various concentrations. Fig. 4 shows that static potential plotted as a function of pH (or pCl) of the solutions examined. Over the range 0.8—2.8 the relation is linear, of slope *ca.* -20 mv/pH unit, and the intercept with the ordinate denotes an e_0 value of 0.160 v, agreeing with that previously reported by Noyes and Chow¹⁴ for the half-reaction (5). This



signifies that in pure hydrochloric acid solutions the electrode potential should change by *ca.* 20 mv for a ten-fold change in hydrogen-ion or chloride-ion concentration. We could then ascribe the relatively low potential values registered over the less regular portion (a) on the potential-pH curves with both protected and unprotected electrodes to the presence of chloride ions in the most acid members of Clark and Lubs's series of buffers used. The deviation from linearity below pH 0.8, shown in Fig. 4, can be ascribed to the instability of the oxychloride phase due to complex formation.¹⁵ Above pH 2.8 the deviation can be ascribed to the formation of some other intermediate phase, such as oxides or hydroxides. Thus for the equilibrium (6) ΔF is -4910 cal./mole. This value



may not be very accurate, yet it does indicate that in acid solutions the oxides disproportionate into BiO^+ ion and metallic bismuth. The ratio $[\text{BiO}^+]/[\text{H}^+]$ will then be approximately $10^{0.9}$. From reaction (3), the variation of the electrode potential as a function of BiO^+ and H^+ ions can be written as

$$\begin{aligned} e &= e_0 + (RT/3F) \log [\text{BiO}^+][\text{H}^+]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7) \\ &= 0.314 + (RT/3F) \log [\text{BiO}^+/\text{H}^+][\text{H}^+]^3 = 0.332 - 0.059 \text{ pH} \end{aligned}$$

The e_0 value found within portion (b) is only 3 mv higher than that denoted by the above equation, which thus offers a satisfactory explanation for the electrode potential behaviour within the pH range 4.0—8.0

The similarity in behaviour of both protected and unprotected bismuth electrodes and the corresponding arsenic and antimony electrodes is thus emphasized. Comparison of the e_0 values in and out of contact with air shows that, in air, the response of the electrode to pH is governed by an oxygen overvoltage effect, which is inhibited by chloride ions in strong acid solutions. Further, as indicated by the results obtained out of contact with air, the stability of the phases involved in the electrode equilibria over the various pH ranges is compatible with that expected from the amphoteric nature of these phases, as will be reported later.

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¹⁴ Noyes and Chow, *ibid.*, 1918, **40**, 739.

¹⁵ Noyes, Hall, and Beattie, *ibid.*, 1917, **39**, 2526.