565. *The Electrochemical Behaviour of the Antimony Electrode.*

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From the discrepancies in the reports on the behaviour of the antimony electode, it is evident that this depends on the prevailing conditions. Recently, the electrode was regarded as irreversible, its potential being governed by an oxygen overvoltage, and it has been called a metal–metal oxide–oxygen electrode.

It is now shown that the irregularities are caused by the gradual formation of a higher oxide (tetroxide) on the electrode and by its exceedingly slow attainment of equilibrium, which depends upon the supply of oxygen as well as on the surface of the metal exposed. The antimony electrode is shown to be a true metal–metal oxide electrode provided that the measurements recorded represent true equilibrium values.

Much work has been carried out on the electrode potential of antimony when immersed in aqueous solutions with a view to its use for the determination of pH. The results of various workers differ widely, and individual values are greatly dependent on the nature of the conditions. Many suggestions as to the cause of this behaviour have been advanced, and although in many cases the presence of dissolved oxygen has been recognised as a fundamental factor influencing the electrode potential, it seems that no attempt has been made to define satisfactorily the real nature of the effect of this gas on the antimony electrode potential.

The behaviour of the antimony electrode (stick and plated) as an indicator electrode for hydrogen ion activity was recently re-examined by Tourky and Mousa (*J.*, 1948, 752); since they found that the E_0 values of their electrodes, as well as those of most previous authors, fluctuated between 0·165 and 0·290 v. as compared with the value of 0·150 v. obtained with the powdered antimony electrode for the system Sb–Sb_2O_3, they concluded that the electrode behaves irreversibly only when in the massive form, its behaviour being governed by an oxygen overvoltage effect due to the persistence on its surface of oxygen doublets. The electrode was therefore called a metal–metal oxide–oxygen electrode.

Some experiments are now reported showing that the antimony electrode, whether in the powdered, massive, or plated form, is reversible; further, that both the fluctuations and the drift observed in the E_0 values by various authors can largely be explained by the gradual formation of a higher oxide (tetroxide) on the electrode and by its exceedingly slow rate of attainment of equilibrium, which depends upon the supply of oxygen and on the surface of metal exposed. When this equilibrium is reached, it corresponds to the reversible value of the system Sb_2O_3–Sb_2O_4. The limits of the applicability of the antimony electrode as an indicator electrode for hydrogen-ion activity are defined, and the importance of obtaining a calibration curve for the electrode before use is emphasised.

EXPERIMENTAL.

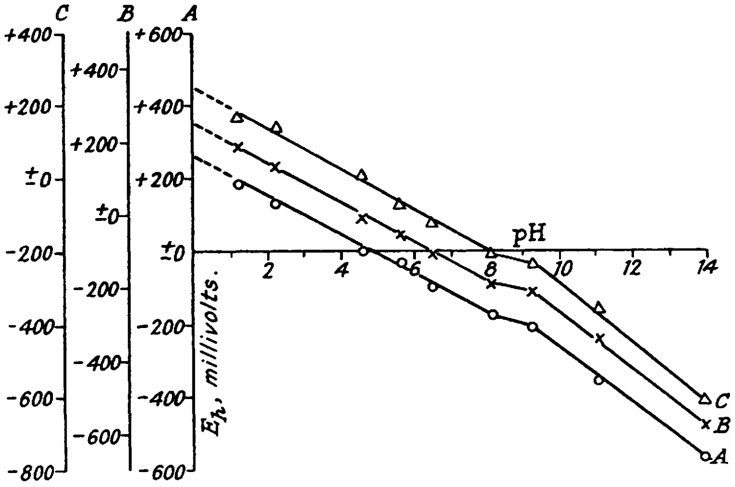
Electrodes.—The antimony electrodes used were of 3 types: (a) *Stick electrode.* This was a rod of pure antimony (B.D.H.) 1·5 cm. long and 0·5 cm. in diameter. (b) *Plated electrode.* This was prepared according to the directions of Shoch and Brown (*J. Amer. Chem. Soc.*, 1916, **38**, 1660); the antimony was deposited on a platinum wire of apparent area 0·05 cm.^{2}. (c) *Powdered electrode.* This was the B.D.H. sample which had been shaken with the solution for some time and then used directly.

The solutions in which the antimony electrodes were examined were buffers covering the pH range 1·2—13·9, *viz.*, potassium chloride–hydrochloric acid, acetic acid–sodium acetate, disodium hydrogen citrate–sodium hydroxide, boric acid–borax, and sodium carbonate–hydrochloric acid buffer mixtures (Britton, "Hydrogen Ions," London 1929, pp. 181 *et seq.*). For the extreme alkaline pH value N-sodium hydroxide was used.

The electrical measurements were carried at 20° ± 0·05°, a saturated calomel electrode being used as the reference half-cell.

RESULTS AND DISCUSSION.

With the three types of electrodes it was possible to differentiate between two potentials, *viz.*, pseudo-equilibrium values which were usually obtained within 3—6 hours, and the steadier values obtained within 72 hours with the massive electrodes and within 120—144 hours with the powder electrode. The pseudo-equilibrium values were approximately the same for the stick and the plated electrode and both were on the average about 0·03—0·05 v. higher than for the powder electrode. In all the cases, the pseudo-equilibrium values slowly became more positive with time. The rate of this drift gradually decreased, becoming fairly constant after the periods noted above. The figure shows the steadier potential–pH curves for the three types of electrode, and it is seen that the potential of the antimony electrode is a linear function of the pH from ~1 to ~8 and then from pH 9 to 13·9. A break always occurred between pH 8 and 9. The E_0 values (values at pH 0) were 0·255, 0·260, and 0·250 v. for the rod, plated, and powder forms, respectively.



A, *Stick antimony electrode.* *B*, *Plated antimony electrode.* *C*, *Powdered antimony electrode.*

The electromotive behaviour of antimony oxides in 0·1N-hydrochloric acid, studied by Hickling and El Wakkad, will be published elsewhere. The results obtained give the following E_0 values for the corresponding systems: Sb–Sb_2O_3 +0·15 v., Sb_2O_3–Sb_2O_4 +0·54 v., Sb_2O_4–Sb_2O_5 +0·59 v., Sb_2O_3–Sb_2O_5 +0·67 v., and it is obvious that the E_0 values obtained with the antimony electrodes are different from any of these.

A survey of the literature on the antimony electrode (see Tourky and Mousa, *loc. cit.*) reveals that only in two out of 23 studies is the E_0 value as low as 0·150 v. Careful examination of these two cases shows that the metal used was in the form of powder and the electrodes as well as the solutions were not freely exposed to atmospheric oxygen. On the other hand, the higher E_0 values were mostly obtained with massive electrodes and in solutions freely exposed to atmospheric oxygen, and in this case a continuous drift with time in a more positive direction was noticed and the E_0 values fluctuated between two widely separated extremes.

The fluctuations in E_0 values and the drift with time suggest that in these cases the measured potentials do not represent final equilibrium. The fact that the drift is in a more positive direction indicates that a higher oxide is being formed and that the disturbance is probably due to the very slow approach of the electrode to its final equilibrium value. This view was further substantiated by measuring the potential of the plated antimony electrode in 0·1N-hydrochloric acid and waiting until the steadier potential was reached; then by bubbling oxygen continuously through the solution, it was found that the drift in potential continued though very slowly towards the more positive direction. For instance, after 3 days the change in potential was ~30 mv., after a week ~40 mv., and after 14 days ~220 mv., so reaching the constant value of 0·490 v. This final potential value agrees satisfactorily with the value of the system Sb_2O_3–Sb_2O_4 at the corresponding pH. It was also noticed, when measuring the potential of the system Sb–Sb_2O_3 in 0·1N-hydrochloric acid and then adding small amounts of either Sb_2O_4 or Sb_2O_5, that the potential varied only by ~90 mv. within the first 24 hours and by ~120 mv. after 42 hours, although the realisation of the systems Sb–Sb_2O_3–Sb_2O_4 or Sb–Sb_2O_3–Sb_2O_5 would necessitate an increase of ~400 or 570 mv., respectively. On the other hand, when powdered antimony was added to Pt–Sb_2O_3–Sb_2O_4 or Pt–Sb_2O_3–Sb_2O_5 the potential at once decreased to ~0·100 v., tending towards that of the Sb–Sb_2O_3 system.

From these observations one can conclude that when the antimony electrode is dipped in aqueous solutions, the trioxide, which is the stable oxide at the surface of the metal, is first formed. This oxide in the presence of oxygen and water can be further oxidised to the tetroxide or the pentoxide (Wulff *et al.*, *Z. Elektrochem.*, 1935, **41**, 542). At the same time the Sb^{IV} and Sb^{V} can be reduced by the metal again to the Sb^{III} state. Thus we have two processes operating at the electrode surface and opposing each other, the first tending to give more positive potential values and the second tending to push it back again to the comparatively negative potential of the trioxide. The rate of the first process is expected to depend upon the amount of oxygen to which the electrode and solution are exposed, and that of the second process depends upon the metallic surface exposed. With the powdered metal, where a comparatively large metallic surface is exposed, the drift is not expected to be appreciable, and when the electrode is not freely exposed to oxygen the potential remains fairly constant at the comparatively negative value of the system Sb–Sb_2O_3. On the other hand, when the metal is in the massive form and in the presence of atmospheric oxygen, a drift will take place and the potential will tend to, but may not, attain the more positive value of the system Sb_2O_3–Sb_2O_4, which, as before, can only be reached after 14 days' bubbling of oxygen. The great variation in the E_0 values obtained by different authors confirms this view, since one would expect that their solutions were differently aerated and that their electrodes differed in shape, and in our view these are important factors affecting the rate of attainment of true equilibrium. This treatment also explains why a calibration curve must always be obtained before the use of the antimony electrode as indicator for hydrogen-ion activity in aerated solutions.

From all these facts it is quite clear that the assumption of the presence of oxygen doublets on the massive antimony electrode is unnecessary and that the antimony electrode is a true metal–metal oxide electrode provided that our measurements represent true equilibrium values. Further, Tourky and Mousa's assumption of the presence of oxygen doublets necessitates that the Sb_2O_3 film formed over the surface of the antimony is unimolecular and very protective, whereas Hickling and El Wakkad's study of the anodic behaviour of antimony showed that the unimolecular film of Sb_2O_3 formed on the surface of the metal is not at all protective and the film reaches a thickness of several molecules.

The break always noticed at about pH 8—9 may be attributed, as in other cases of potential–pH curves of metal–metal oxide electrodes (Tourky and El Wakkad *J.*, 1948, 740; El Wakkad and Salem, *J. Phys. Colloid Chem.*, 1950, in the press), to the position of the isoelectric point of Sb_2O_3, which lies at about pH 8·6 (Tourky and Mousa, *J.*, 1948, 755). Tourky and Mousa (*loc. cit.*, p. 758) attributed the breaks in their potential–pH curves to different types of dissociation of $Sb(OH)_3$. Such an assumption, however, is not justifiable since, whatever the kind of the dissociation of $Sb(OH)_3$, so long as the different ionic species are in equilibrium with each other the potential must be the same. Only at the isoelectric point, where the oxide or hydroxide can be considered as dissociating neither as acid nor as base, can one expect anomalous behaviour: before or after this, the normal trend of the potential–pH curves of the metal–metal oxide must exist.

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