149. *Studies on Some Metal Electrodes. Part IV. The Behaviour of the Antimony Electrode out of Contact with Air.*

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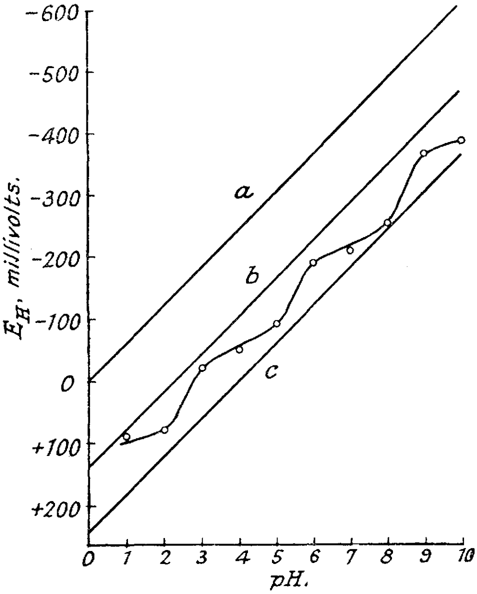
Examination of the behaviour of antimony electrodes prepared by electrodeposition and subjected alternately to hydrogen gas and to high vacuum at ~350° in buffer solutions of pH 1—10 shows that equilibrium values are quickly attained which remain constant for several hours. The potential–pH curves obtained consist of four parallel lines separated from each other by steeper slopes starting at about pH 2, 5, and 8. In the light of the amphoteric properties of antimony trioxide (see following paper), the curve is regarded as a titration curve, first of the triacid base and then of the monobasic acid. From this and other observed phenomena, the conclusion is drawn that, by the process of reduction, only those oxygen doubtlets leading to the overvoltage effect in air are removed but not the underlying layer of the trioxide. The results obtained with the electrode out of contact with air substantiate further the suggestion that in air the electrode is governed by an overvoltage effect due to the presence on its surface of oxygen doublets. These when present mask the amphoteric properties of the trioxide and lead to a straight potential–pH relationship as that based on the steady state values.

In Part III (preceding paper), it was suggested that massive and electrodeposited antimony electrodes behaved in air as metal–metal oxide–oxygen rather than as metal–metal oxide electrodes. The variation in potential with time and the straight potential–pH relationship as based on the first steady state values, and also the values of E_0' higher by ~100 mv. than the thermodynamic one when working with these electrodes, all could be explained by assuming the presence on the electrode surface of oxygen doublets leading to an oxygen overvoltage effect. The object of the present work was to find out whether further substantiation for the theory could be obtained by studying the behaviour of the electrode in the same set of buffers as those used in Part III but after it had been subjected alternately to the reducing action of hydrogen and to high vacuum. By this treatment the complexity of the surface structure leading to the peculiar behaviour of the electrode in air might be reduced, with the result that it would manifest only such properties as could be expected from a homogeneous surface field.

EXPERIMENTAL.

The antimony electrodes were prepared by electrodeposition as in Part III (*loc. cit.*) on platinum plates that were sealed into electrode jackets such as were used in Part I (this vol., p. 740); the procedures adopted for purifying hydrogen, reduction, evacuation, and exclusion of oxygen from the solutions were also essentially the same. In order to ascertain that the process led to reproducible conditions on the electrode surface, some electrodes were subjected to different treatments with respect to the time of exposure to hydrogen and high vacuum within the temperature range 300—400° and were then examined in the same buffers. It was found that electrodes heated three times alternately in the presence of hydrogen for 4 hours and subjected to vacuum for 1 hour gave practically identical results with electrodes heated alternately for 6 hours and subjected to vacuum each time for 2 hours at 350°. This temperature was also considered high enough to exclude the possibility of formation of stibine, which decomposes completely at 150° (Stock and Doht, *Ber.*, 1901, **34**, 2339). The buffer solutions were the same as those used in the previous paper.



Results.—With antimony electrodes prepared and treated as above, equilibrium values were attained in all buffers within 15—20 minutes which remained practically constant for the next 20 hours, the time limit of experiments. The maximum deviation recorded during that period was only $\sim$11 mv. at about the neutral point. By plotting the potentials attained after equal periods of time against pH, curves were obtained such as that shown in the figure, which instead of being a single straight line consisted of four parallel lines separated from each other by steeper slopes starting at about pH 2, 5, and 8. The first portion of the curve representing the measurements up to about pH 2 was not quite regular; the other three portions had slopes of 34·1, 32·4, and 23·2 as compared with the values of 100·1, 98·4, and 109·6 v. respectively for the steeper inflections.

DISCUSSION.

Practically every metal becomes coated with an oxide film when exposed to air. Realising that compact film growth on a variety of metals is brought about mainly through the diffusion of metal ions and electrons through the oxide lattice towards the solid–gas interface, Jost (" Diffusion und chemische Reaktion in festen Stoffen ", Dresden and Leipzig, 1937; Ann Arbor, Michigan, 1943, p. 149), Price (*Chem. and Ind.*, 1937, **56**, 769), and Hoar and Price (*Trans. Faraday Soc.*, 1938, **34**, 867) conceived a metallic surface undergoing oxidation as a current-producing cell with the metal, film, and film-attacking substance interfaces as cathode and anode respectively, the film being both electrolyte and external circuit. Oxide films on metals such as copper or iron at room temperature attain considerable thicknesses and it is not necessary to assume other mechanisms than the above for their growth, provided that they remain free from holes and cracks. Compact oxide films on metals such as aluminium, on the other hand, attain thicknesses not exceeding 50—100 A. owing to their impermeability to metal ions and, above a certain thickness, to electrons unless these receive a thermal energy of activation (Mott, *ibid.*, 1940, **36**, 472). The impermeability of such films manifests itself in the exceedingly low conductivity of the oxide in bulk (Hoar and Price, *loc. cit.*, p. 871) and is considered to be connected with the nature and extent of deviations from a strict order of an ideal ionic lattice in the oxide (Wagner, *Z. physikal. Chem.*, 1933, *B*, **21**, 25; Grünewald, *ibid.*, 1938, **40**, 455; Wagner, *Trans. Faraday Soc.*, 1938, **34**, 851), its crystalline form, and its orientation with respect to the substrate (Barrer, " Diffusion in and through Solids ", Cambridge, 1941,

p. 276). Diffusion anisotropy, *i.e.*, diffusion occurring with different velocities along different crystallographic axes, is not observed in cubic crystals but is to be expected in systems with lower symmetry.

The work hitherto done on tarnishing reactions is limited—as far as the authors are aware—to but a few metals, not including antimony. However, one can obtain an approximate picture of what may be expected to occur when this metal oxidises as follows: The facts that the volume quotient of Sb_2O_3/Sb is 1·50 (Fischbeck, *Z. Elektrochem.*, 1933, **39**, 316) and that there is an increase in the density of the oxide only by ~8% when it is transformed by uptake of oxygen into the tetroxide (Simon, *Z. anorg. Chem.*, 1927, **165**, 31) imply that a compact film on the metal will be practically impermeable to oxygen molecules and that film growth—if there be any—should mainly be effected through the diffusion of metal ions and electrons towards the solid–gas interface. Such diffusion is, however, not to be expected, since according to a general rule (Jost, *op. cit.*, p. 79), in solids composed of ions of different charges, those ions will diffuse which possess the lower charge, *i.e.*, in the case under consideration the diffusion should be limited to the slow-moving oxygen ions, a process which cannot contribute to film growth on the metal. The rule, which is based in observations on the diffusibility through a variety of salts, has recently found confirmation in the tracing of oxygen-lattice defects in the mixed crystals of $CeO_2 + La_2O_3$ and $PbO + Bi_2O_3$ (Zintl and Croatto, *Z. anorg. Chem.*, 1939, **242**, 79; Sillen and Aurivillius, *Naturwiss.*, 1939, **27**, 388), which indicates that analogous defects may be found in simpler lattices (Wagner, "Handbuch der Metallphysik", Leipzig, 1940; Ann Arbor, 1944, p. 133).

The foregoing discussion shows that antimony tends to become passivated when exposed to atmospheric oxygen owing to the impermeability of the film formed on its surface to oxygen molecules and to the non-diffusion through it of metal ions towards the metal oxide–gas interface. In contradistinction, with a metal such as copper, a compact oxide layer formed on its surface will not attain considerable thickness, and any oxygen molecules adhering to such a layer may remain as doublets for varying periods of time. In air the electrodic behaviour could be satisfactorily explained by assuming the presence on its surface of oxygen doublets, the formation of which, though quite feasible in the light of the statements made above about the mechanism of oxidation of antimony, is further substantiated by the behaviour of the electrode out of contact with air.

As stated above, equilibrium values are quickly attained after immersion in almost all buffers (and these remain constant for several hours) when the electrode is subjected alternately to hydrogen and to a high vacuum at ~350°. Taking into consideration the restrictions imposed on the process $Sb^{3+} + 3e = Sb$, which renders antimony an irreversible metal electrode as compared, *e.g.*, with silver, the deposition potential of which is not far removed from its dissolution potential, the constancy of the potentials observed can only be attributed to a metal–metal oxide electrodic behaviour. This contention is borne out by the fact that on drawing the best straight line through the points in the figure, the ordinate is intersected at a value approaching more the thermodynamic than the value higher by ~100 mv. for the system $Sb–Sb_2O_3–OH'$ in air. The stepwise trend of the potential–pH curve obtained by connecting all points can also be accounted for by assuming the presence of antimony trioxide on the metal surface. This (see Part V) behaves mainly as an ortho-base below, and as a meta-acid above, its isoelectric point at ~pH 9. The curve with its inflections at the pH values 2, 5, and 8 respectively can therefore be regarded as a titration curve first of the triacid base, the dissociation constants of which lie apparently far apart from each other, and then of the monobasic acid.

By successively subjecting the antimony electrode to hydrogen and to high vacuum at ~350°, only those oxygen doublets which govern the electrodic behaviour in air, making its potential at the steady state more positive by ~100 mv. at 30°, are therefore removed, but not the underlying layer of the oxide. This, although quite reducible when in the bulk phase, under the given experimental conditions apparently resists the action of hydrogen when forming a continuation of the metal lattice.

In the light of the results obtained with the electrode out of contact with air, the behaviour of the massive or electrolytically deposited antimony electrode in air can now be visualised as follows: Owing to the restrictions imposed on the growth of an oxide layer on the metal, leading to the formation of oxygen doublets, the electrodic process will be governed by an oxygen overvoltage, and all properties relating to the amphoteric nature of the oxide will be masked when the doublets cover practically completely the whole metal surface. This condition is apparently satisfied within 1—2 hours at the first steady states which are related to pH through a straight line. After longer periods of immersion (20—24 hours) the properties of the oxide manifest themselves more pronouncedly, probably owing to its further development by the local action process. The curve as shown in Fig. 2 of Part III bears some resemblance to the curve obtained out of contact with air but indicates that the electrodic behaviour is still governed by an oxygen overvoltage even after this elapse of time.

In contradistinction to copper, which functions within a certain pH range as a metal–metal oxide electrode, the antimony electrode does not lead to a straight potential–pH relationship unless it is properly governed by an oxygen overvoltage. As such, the electrode may be labelled as a metal–metal oxide–oxygen electrode in order to emphasise its properties as distinguished from those of metal–metal oxide electrodes such as copper or the protected antimony electrode.

Vogel (*Congr. Chim. Ind. Bruxelles,* 1935, **15**, II, 1068), with a massive electrode in air-saturated solutions, obtained a curve consisting of three parallel lines with the inflections at pH 5 and 7·5, which he ascribed to the occurrence in solution in contact with the metal of the three successive states of oxidation represented by SbO^+, Sb^{3+} and Sb^{5+}. In the light of the present investigation his explanation appears unnecessary.

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