282. *Studies on Some Metal Electrodes. Part VII. The Behaviour of Arsenic Electrodes prepared by Sublimation and Decomposition of Arsine out of Contact with Air.*

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Electrodes prepared by sublimation of arsenic or decomposing arsine in an atmosphere of pure hydrogen are found to behave similarly to each other. The potential–pH curves initially obtained bear considerable analogy to those found in air with massive electrodes with the difference, however, that the overvoltage effect decayed within a few hours, whereby the thermodynamic potentials were ultimately obtained. This remarkable phenomenon is attributed to a mechanism involving the discharge of hydroxyl ions on the clean metal surface to oxygen atoms which partly combine to form oxygen molecules and partly penetrate as such through the oxide film, leading to its further development and subsequently to the rapid depolarisation effect. The mechanism throws light on the process leading to the charging of an electrode surface in general, and explains satisfactorily the behaviour of antimony or arsenic electrodes involving the powdered metal in air.

Owing to the fact that it can be readily sublimed or obtained by the decomposition of suitable volatile products such as arsine, arsenic is one of the few metals that can be obtained free from oxide or absorbed oxygen. By carefully excluding oxygen during the deposition of the metal and from the test solutions, one can then obtain information regarding the mechanism of the electrode process of a metal with a clean surface. Such a condition was not satisfied with antimony electrodes prepared by electrolytic deposition and alternately subjected to the action of hydrogen and to high vacuum at $\sim$350°, whereby only the labile oxygen film was removed but not the underlying layer of oxide. From the time of immersion, the potentials set up did not vary with time and the pH–potential curves were characterised by inflections corresponding to the titration of antimony trioxide first as an ortho-base and then as a meta-acid. In the present investigation, we report the behaviour of arsenic electrodes which were prepared by the two methods, *viz.*, sublimation of the metal in presence of hydrogen under conditions permitting only the deposition of the crystalline form, followed by degassing the metal under high vacuum, and decomposing arsine in the complete absence of oxygen.

Experimental.

(A) *Preparation of the Electrodes by Sublimation.*—In following this procedure it was taken into consideration that hydrogen gas does not dissolve in the metal or lead under ordinary conditions to the formation of any compound (Fresenius and Babo, *Annalen*, 1844, **49**, 305; Reckleben and Scheiber, *Z. anorg. Chem.*, 1911, **70**, 255). The process involved the following steps.

(i) The powdered metal was heated for a sufficient time at 180—190° under a circulating atmosphere of pure hydrogen. The choice of this temperature range was based on the fact that the heat of formation of the octahedral oxide which is liable to be formed on the metal is 156,400 cals. (Bischowsky and Rossini, "Thermochemistry of Chemical Substances," New York, 1936, p. 40) and its reduction with hydrogen should be possible at 192° (St. John, *J. Physical Chem.*, 1929, **33**, 1438); further, that below this range, the oxide volatilises appreciably (Selmi, *Mem. Accad. Bologna*, 1878, **9**, 133) and at higher temperatures it may be transformed into the less volatile glassy form. (ii) The metal was sublimed in presence of hydrogen under conditions permitting only the deposition of the stable form. (iii) The deposited metal was degassed under a high vacuum.

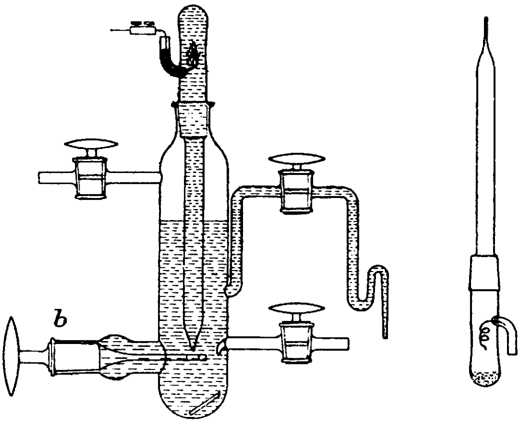
The experiments were started by introducing some powdered arsenic from one of the sublimation columns into the electrode jacket, which was then sealed into a high-vacuum device surrounded with an electric heating-oven packed with asbestos. After thorough evacuation, as could be judged by a McLeod gauge, hydrogen [purified by the method of Hönigschmid *et al.* (*Z. anorg. Chem.*, 1927, **163**, 78)] was then gradually admitted and made to circulate with the aid of a mercury oscillating pump. Meanwhile, the temperature of the oven was raised to 180—190°, in which range the electrode jacket with the powdered metal was left for 30 minutes in the circulating hydrogen. The operation of evacuation and introducing new supplies of hydrogen was repeated at least 3 times before the device was allowed to attain the laboratory temperature in presence of hydrogen. The next steps involved drawing the narrow end of the electrode jacket (Fig. 1) to form a fine capillary, placing the heating oven about 1 cm. above the platinum spiral and maintaining it at 380°, and finally subliming the metal in presence of hydrogen with the aid of a micro-Bunsen burner so as to deposit it on the spiral in the form of bright metallic clusters.

After thorough evacuation, the electrode jacket was sealed off at the capillary constriction and carefully fitted into the electrode vessel holding the buffer solution, previously freed from any dissolved oxygen by bubbling in nitrogen purified according to Harcourt and Lupton (*Chem. News*, 1876, **33**, 90). When the tip of the capillary constriction was broken the buffer bathed the electrode and the measurements could then be made.

(B) *Preparation of Arsenic by Formation and Decomposition of Arsine.*—For the preparation of arsine a modified form of Robertson's apparatus (*Proc. Roy. Soc.*, 1928, **120**, 160) was used, and the arsine was prepared by the action of a solution of arsenious oxide in freshly boiled hydrochloric acid on pure magnesium turnings (Robinson *et al.*, *J.*, 1934, 730). This process as well as the process of decomposing the product could both be performed out of contact with air in a closed system that could be subjected to a high vacuum.

Electrodes prepared by method (A) were examined in Clark and Lubs's buffer solutions covering the pH range 1—10. Those prepared by method (B) were examined in the same buffers but only of the pH values 0·97, 3·00, 5·03, 6·99, and 8·95. All experimental details concerning the preparation of the buffers and the measurements were the same as described in previous papers.

Fig. 1.



Results and Discussion.

In Fig. 2 are shown the log time–potential curves obtained with arsenic electrodes prepared by sublimation in presence of hydrogen. Essentially similar curves were obtained with electrodes prepared by decomposing arsine, thus indicating the reproducibility of the results for electrodes initially free from an oxide film or absorbed oxygen. As can be seen in all buffers except the most alkaline ones, the potentials set up on immersion decrease appreciably with time towards the thermodynamic values for the As–As_2O_3 system.

Fig. 2.

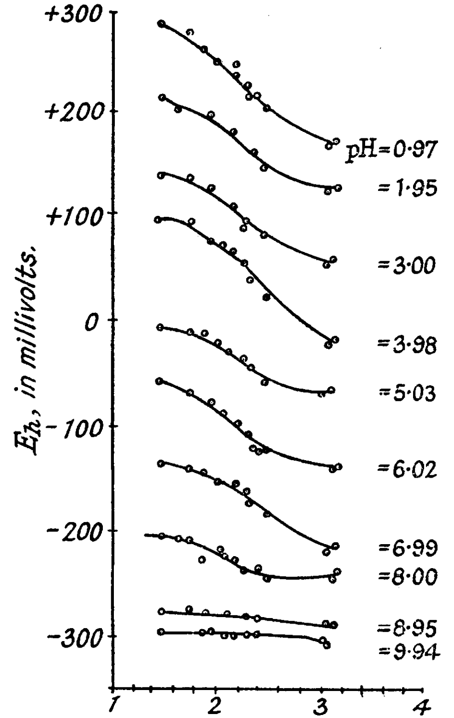
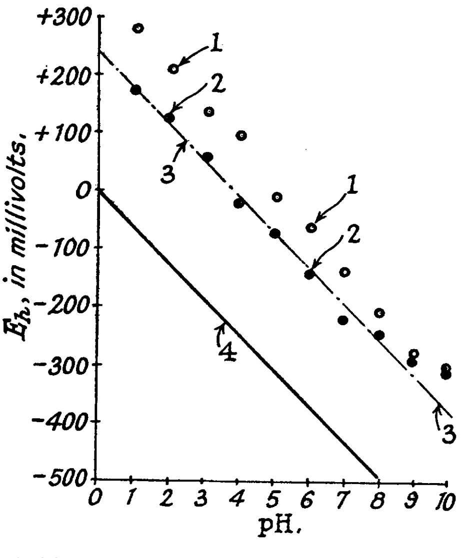


Fig. 3.



(1) *Initial potentials* (~30 *minutes after immersion*).
(2) *Final* ,, (~20 *hours* ,,).
(3) *Reversible* As–As_2O_3 *system.*
(4) ,, *hydrogen electrode system.*

Fig. 3 representing the pH–potential plots based on the initial (30 minutes) and the final (48 hours) potentials reveals that both curves bear considerable analogy to the pH–potential plots obtained in air—the former to those manifested with massive arsenic electrodes in conjunction with the trioxide, which was found to be governed by an oxygen overvoltage effect, and the latter to those obtained with electrode systems involving the powdered metal. The question which now arises pertains to the factors leading to the overvoltage effect out of contact with air and to its more or less rapid decay. It has been assumed by earlier workers (Heyrovsky, *Proc. Roy. Soc.*, 1923, **102**, 628; Kistiakovsky, *Z. physikal. Chem.*, 1910, **70**, 206; Reichinstein, *ibid.*, 1920, **95**, 457) that the primary process leading to the charging of an electrode surface of a metal M was not, for example, $M \longrightarrow M^{++} + 2e$, but was probably due to reactions such as $M + O^{--} = MO + 2e$ or $M + 2OH^- = M(OH)_2 + 2e$. Kinetically it is difficult to ascribe the process to a reaction with oxygen ions owing to the negligible quantity of these in aqueous solutions (Bjerrum, *ibid.*, 1923, **106**, 230); nor, in the light of the present results, can it be ascribed to a simple interaction with hydroxyl ions, for otherwise the overvoltage effect initially observed remains unexplained. A more plausible theory for the charging process is that the reaction $2OH^- \longrightarrow H_2O + O + 2e$ proceeds at the clean metal surface and is the more stimulated the stronger the alkalinity of the solution, with the result that the oxygen atoms formed partly combine with the metal to form the oxide and partly aggregate to form oxygen molecules. The latter process depends on several factors, one of which is the mobility of these atoms on the electrode surface. If all atoms formed were capable of forming oxygen molecules, a persistent overvoltage effect would result owing to the impermeability of the film initially formed for the same reasons as those adduced in the case of the antimony electrodes. If, on the other hand, part of the oxygen atoms were capable of penetrating through the film—which is likely to be the case—the oxide will continuously develop on the electrode, disaggregating in its neighbourhood and depolarizing the overvoltage effect caused by the absorbed molecules. There is thus a marked difference between the effects caused by oxygen deposited from the gas phase and that formed by the discharge of hydroxyl ions, and this affects the mechanism leading to the attainment of the thermodynamic potentials with electrodes involving the powdered metal. As was shown in the previous paper, straight pH–potential relationships were only obtained when the electrode systems involved arsenious oxide in addition to the powdered metal. Electrodes consisting only of the powdered metal yielded points lying mostly somewhat above the theoretical plot on the acid side of pH 7 and behave in this respect similarly to electrodes of the massive type out of contact with air at the initial stage after immersion. An approach to the problem of the behaviour of these and of the similar antimony electrodes in the powdered form may be obtained by considering the mechanism underlying crystal growth in general. It has been recognised that the building up of a new particle (ion, atom or molecule) is associated with the release of varying amounts of bonding energy according to whether it becomes attached to an edge, a corner, or a plane on the crystal, and further, as to whether by the process a new lattice plane is started or is completed or the particle merely adds to others in an uncompleted plane (Volmer, "Kinetik der Phasenbildung," Leipzig, 1939; Ann Arbor, Mich., 1945, pp. 32 *et seq.*). Since, before their allocation in fixed positions, the particles possess considerable mobility (Volmer, *op. cit.*), their allocation will be governed by a Maxwell–Boltzman distribution law and points will be left unoccupied which possess considerable bonding energy. It is these active points, the frequent occurrence of which is to be expected in electrode systems involving the powdered metal, which catalyse the above or other similar reactions whereby the oxygen atoms released will play the same rôle as already outlined. Other catalytic reactions brought about by oxides have been explained on similar lines (Schwab, *Z. physikal. Chem.*, 1929, *B*, **5**, 406; Cremer and Schwab, *ibid.*, 1929, *A*, **144**, 243).

Another feature of the results obtained with arsenic electrodes out of contact with air is that they seem to provide some experimental evidence supporting Fowler's views on overvoltage. As he pointed out (*Trans. Faraday Soc.*, 1932, **28**, 368), overvoltage phenomena in general are to be regarded rather as primary and essential for the passage of appreciable currents, and they are not in any way due to secondary effects such as the need to overcome the resistance of obstructive layers of gas as has been argued.

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