281. *Studies on Some Metal Electrodes. Part VI. The Arsenic Electrode as a Metal–Metal Oxide–Oxygen Electrode.*

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By examining massive arsenic electrodes in buffers of different pH in air, it is found that, although the straight portions of the pH–potential curves obtained are almost parallel to the line representing the variation of the hydrogen electrode potential with pH, yet they are characterised by E_0' values approximately 0·1 volt more positive than that theoretically derived for the As–As_2O_3 system. A value approaching the theoretical one is only obtained on using electrode systems involving the powdered metal. It is shown by experiment that the shift in potential cannot be ascribed to the nature of the deposited metal, to the participation of some higher oxides in the electrode equilibrium, or to alloy formation between arsenic and platinum when the latter is used as substrate. The possibilty of explaining such abnormally high positive potentials in terms of concentration polarisation is also excluded. A valid explanation is that the massive arsenic electrode is governed by an oxygen overvoltage effect and, like the antimony electrode, behaves as a metal–metal oxide–oxygen rather than as a metal–metal oxide electrode.

It has been shown in Parts III, IV, V (*J.*, 1948, 752, 756, 759) that the behaviour of the antimony electrode in air can be satisfactorily accounted for in the light of the modern theory of lattice defects as applied to the oxide formed on the metal. Owing to the impermeability of the initially formed film to oxygen molecules and to the non-diffusion through it of the metal ions towards the solid–gas interphase, a layer of oxygen doublets persists on the electrode surface leading to an overvoltage effect of about 0·1 volt which is superposed on the thermodynamic potential. By subjecting the electrode alternately to hydrogen and to high vacuum, the layer of oxygen is removed and the behaviour of the electrode is governed only by the trioxide. In the present investigation results of measurements with arsenic electrodes of different types and under a variety of conditions are recorded which not only substantiate the theory previously outlined but indicate that the arsenic electrode, not yet adequately studied, is better than the antimony electrode for measuring pH.

EXPERIMENTAL.

Preparation of Metallic Arsenic.—The standard state of arsenic is the solid metallic α-form. There are also the yellow, cubic, low-density γ-form and some varieties formerly regarded as amorphous, but now known (Cohen and Olie, *Z. physikal. Chem.*, 1910, **71**, 1) to be solid solutions of the other two forms. In the present investigation, only α-arsenic was used; it was prepared by reduction of pure arsenious oxide with sugar-charcoal in an atmosphere of carbon dioxide (cf. Lenan *et al.*, *Phil. Mag.*, 1928, **6**, 666). The metal was powdered and resublimed in portions in pure nitrogen in especially devised columns at ~350°, a temperature high enough to cause the irreversible transformation of any unstable forms into the stable one (Stöhr, *Z. anorg. Chem.*, 1939, **242**, 44, 138). The metal, which was deposited in glistering clusters, left no residue after sublimation. The inlet and outlet for nitrogen were then sealed off while the gas was circulating so as to minimise oxidation of the element pending its use.

FIG. 1.

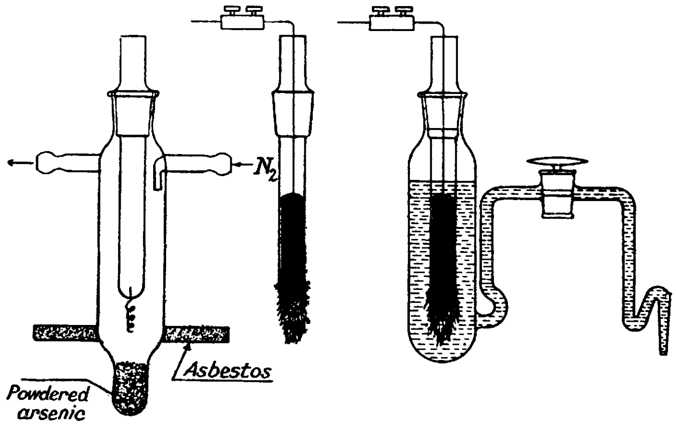
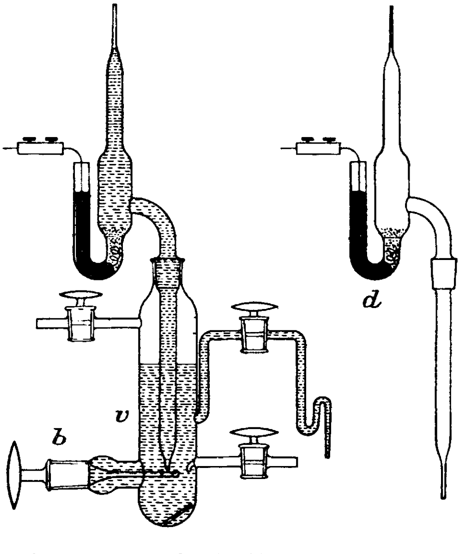


FIG. 2.



Electrodes.—These consisted of the freshly prepared massive or powdered metal, singly or in conjunction with each other, and with or without the stable octahedral or the unstable vitreous form of arsenious oxide. Fig. 1 shows how electrodes of the massive metal are prepared by sublimation and employed. Fig. 2 represents a device for electrodes made of the powdered metal with or without the oxide. It consists of the part *v* to hold the buffer, which should be presaturated with the oxide when this is used, and the part *d* to contain the powdered material. By gentle tapping, the powder can be well packed round a platinum spiral sealed into the U-tube and serving as lead to the mercury contact. After being evacuated and sealed off at its upper and its lower end, *d* is fitted tightly into *v* with its capillary end passing through *b*, which when turned serves to break the seal and thus to fill *d*. The forms of the oxide used were prepared as described in Part VIII (this vol., p. 1305). The buffer solutions were prepared and the measurements performed as in previous parts of this series (*loc. cit.*).

RESULTS AND DISCUSSION.

Series A : Electrodes consisting of the Massive Metal.—Types of electrode. Freshly prepared massive electrodes obtained by sublimation and deposition on platinum, the deposit being renewed before each set of measurements in any one buffer, are referred to as type A_I, and A_{II} represents electrodes prepared as above but left to age in air for *ca.* 12 months.

Electrodes of the type A_I set up potentials which were very sensitive to changes in pH. Comparison of the initial values obtained after ~30 minutes in each buffer with those obtained after ~70 hours shows that, up to pH 7, there is but a slight tendency in almost all buffers to acquire less positive values with time. Above pH 7, the final potentials are always more positive than the initial ones. By plotting the initial and final potentials against pH, curves representing straight lines within the approximate pH ranges 3—10 and 4—9, respectively, are obtained (see Fig. 3). The E_0' values calculated in each case are 0·3399 and 0·3320 volt and are thus about 0·1 volt more positive than the reversible one (see below).

Electrodes of type A_{II} behave similarly, but the final potentials on the whole are less positive than the corresponding ones of A_I. The reproducibility of the pH ranges as well as the relations representing the straight lines are, however, less definite with these electrodes than with the other type or with systems involving the oxide.

Series B : Electrodes consisting of the Massive Metal in Conjunction with Arsenious Oxide.—Types of electrode. B_I and B_{II} represent freshly prepared massive electrodes in conjunction with the stable octahedral and with the vitreous form of the oxide, respectively.

The tendency of these electrodes to acquire, with time, less positive potentials below, and more positive ones above, pH 7 is much more marked than with electrodes of the former types. The potentials on the alkaline side of pH 7 fall more nearly on the straight lines after longer immersion periods. The pH–potential curves constructed on the basis of either initial or final potentials are again straight lines, but in this instance only within the approximate pH range 4—7, above which they flatten.

Electrodes of the type B_{II} show analogous behaviour save for the greater extent of flattening of the pH-potential curves above pH 7. The E_0' values obtained with both types of electrode approach very closely those obtained with electrodes of the A types.

Series C : Electrodes involving the Powdered Metal.—Types of electrode. Type C_I represents electrodes consisting of the powdered metal only, and C_{II} those consisting of both powder and massive metal; C_{III} and C_{IV} are the same as C_I and C_{II}, respectively, but with the octahedral oxide.

The potentials set up with these types of electrode on immersion are on the whole about 0·1 volt less than those set up by electrodes of series A or B in the corresponding buffer solutions. The initial and final potentials in particular with electrodes involving the oxide were very close to each other and showed but slight variation with time. By plotting both initial and final values with electrodes of the types C_I and C_{II} against pH, straight lines are not obtained, though the best straight line would divide the points into sets lying slightly above or below it on the acid and the alkaline side of about pH 7, respectively, and coincides fairly closely with the theoretical plot for the $As–As_2O_3$ system. By plotting the potentials obtained after 30 minutes with electrodes of the types C_{III} and C_{IV} against pH, straight lines within the approximate pH range 1—7 are obtained with E_0' values closely approaching the thermodynamic one. Above pH 7, all curves tend to flatten towards more positive values as with all types of electrode involving the oxide. Fig. 3 shows the pH–potential plots obtained with the different types of electrode.

One of us (A. A. M.) will report elsewhere how, in the light of the above and other studies, the freshly deposited arsenic electrode, not hitherto used, may with advantage replace the antimony electrode for determining pH, and in Part VIII, on the basis of the amphoteric and other properties of arsenious trioxide, we interpret the pH–potential plots. For elucidating the theory underlying the functioning of the electrode it remains, however, necessary to ascertain that the lower E_0' value actually represents the thermodynamic one and that the higher values can only be attributed to the oxygen over-voltage effect operating on the massive electrodes.

(A) *The Thermodynamic Potentials of the* $As–As_2O_3$ *and the* $As–As_2O_5$ *System.*—It has been suggested that in the presence of oxygen and moisture, arsenic is superficially transformed into the trioxide. There is, however, the possibility that the pentoxide as well might be formed, and the two electrode reactions may be represented, respectively, by

$$2As + 6OH' = As_2O_3 + 3H_2O + 6e \quad \text{. . . . .} \quad (1)$$

and

$$2As + 10OH' = As_2O_5 + 5H_2O + 10e \quad \text{. . . . .} \quad (2)$$

From a knowledge of the free energy of formation of each of the reactants and resultants, the net free-energy change ΔF of each of the above reactions and hence the reversible potentials of each of the electrode systems $As–As_2O_3$ and $As–As_2O_5$ may be computed.

The free energy of formation of As_2O_3 at 35° as computed from the relation $\Delta F = \Delta H - T\Delta S$ is 137,457 cals. when ΔH is taken equal to 156,400 cals. ("High-temperature Specific Heat Equations for Inorganic Substances," *Bur. Mines Bull.*, 1934, p. 371) and ΔS equal to 64·73. For calculating the latter value, entropy values at 298·1° K. for arsenious oxide, oxygen, and elementary arsenic of 25·6, 49·03, and 8·40, respectively, were used, which by integration between 298·1° and 308·1° K. yield the values 26·41, 29·27, and 8·61, respectively. The free energy of formation of water and the hydroxyl ion at 35° can be derived from the relations:

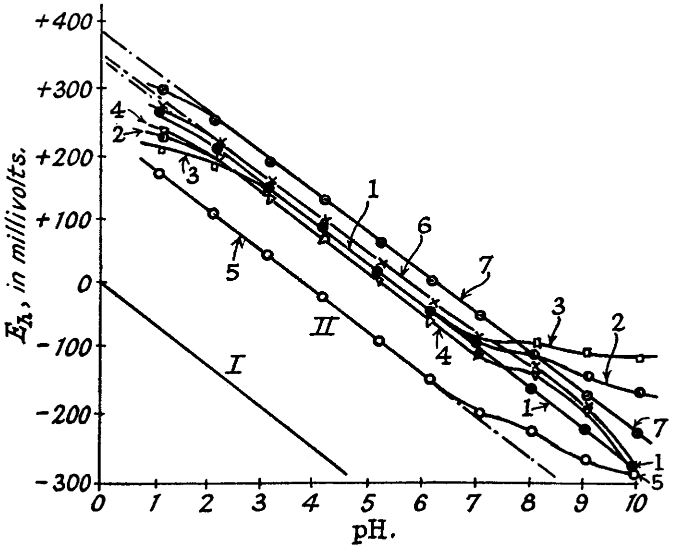
$$H_2 + \frac{1}{2}O_2 = H_2O;\ \Delta F = 56{,}560 \text{ cals. at } 25° \qquad (3)$$

and

$$H_2O = H^+ + OH^-;\ \Delta F = -19{,}105 \text{ cals. at } 25° \qquad (4)$$

The free energy of reaction (3) at 35° as computed from the oxygen–hydrogen cell, given by Nernst and Wartenberg as $1·232 - 0·00085(t - 17)$ volts, is 56,143 cals. That of reaction (4) is found to be −19,278 cals. at 35°, as calculated from the relation, log $K_w = -$ $\boldsymbol{R}T$ log K_w, where K_w, the ionic product of water at 35°, is obtained from Harned and Hammer's relation (*J. Amer. Chem. Soc.*, 1933, **55**, 2194), log $K_w = -4787/T - 7·1321 \log T - 0·010365T + 22·801$, applicable between 0° and 60°. By combining equations (3) and (4), the free energy of the hydroxyl ion at 35° is found to be 36,865 cals.

FIG. 3.



(1) *Freshly deposited massive electrode at* 35° (*no oxide*).
(2) *Same, but with the octahedral oxide.*
(3) ,, ,, *vitreous* ,,
(4) *Electrode after* 11 *months' ageing.*
(5) *Electrodes involving powdered metal.*
(6) *Fresh massive electrode under oxygen atmosphere.*
(7) ,, ,, *at* 20°.

I.—*Reversible hydrogen electrode system.* II.—*Reversible* $As{-}As_2O_3$ *system.*

When arsenic is in its standard state, its free energy of formation is zero. Accordingly, ΔF of reaction (1) is 83,696 cals., and the reversible potential of the electrode system $As{-}As_2O_3$ is −0·605 v. The potential of the hydrogen electrode in a solution containing hydroxyl ions at unit activity, computed as shown above from the reaction $H^+ + OH^- = H_2O + e$, is +0·836 v. The difference in potentials denoting the magnitude of the term E_0' of the $As{-}As_2O_3$ system is therefore 0·231 v. at 35°.

By proceeding in an analogous manner, 218,300 cals. being taken as the value for the heat of formation of As_2O_5 (de Passille, *Ann. Chim.*, 1936, **5**, 83), the E_0' term of the $As{-}As_2O_5$ system is found to be 0·425 v. at 35°. The former value agrees very closely with those registered with electrodes involving the powdered metal (type C) and are about 0·1 volt less than those obtained with electrodes of the types A or B.

(B) *The Effect of Other Factors on the Positive Shift observed with Massive Electrodes.*—(i) *Nature of the deposited metal and possible alloy-formation.* By examining the behaviour of a large arsenic crystal on the one hand and of the deposited metal on the other in a buffer solution of pH 3, Gatty and Spooner ("Electrode Potential Behaviour of Corroding Metals," Oxford, 1938, p. 367) attributed the higher positive potentials observed by Kruger and Kahlenberg (*Trans. Amer. Electrochem. Soc.*, 1930, **58**, 341) than those obtained by Schuhmann (*J. Amer. Chem. Soc.*, 1924, **46**, 1444) to the variable state of the metal and to local action processes on the electrode surface. As this conclusion could only be justified if measurements were made at pH values leading to a linear pH–potential plot, single crystals prepared as recommended by those authors were examined throughout the whole pH range, whereby it was found that they behave in the same manner as electrodes of type A_I. Analogously, it was found that the positive shift could not be ascribed to alloy formation between arsenic and the platinum substrate, since deposition on copper, nickel, or steel did not show any peculiar behaviour that would indicate alloy formation, at least under the conditions prevailing during deposition. Alloy formation with platinum only occurs at *ca.* 600° (Friedrick and Leroux, *Mettallurgie*, 1908, **5**, 148), an arsenide with an average content of 87·04% Pt being formed. With this alloy, the pH–potential curve was an almost straight line denoting an E_0' value equal to about 0·800 v. as compared with the value of 0·980 v. reported by Furman (*J. Amer. Chem. Soc.*, 1922, **44**, 2685) for the potential of bare platinum in aerated aqueous solutions.

(ii) *Participation of higher oxides.* The fact that the E_0' values obtained with arsenic electrodes of the massive type lie between those of the As–As_2O_3 and of the As–As_2O_5 system might indicate at first sight that the electrodic behaviour is governed by a mixture of both oxides. This, however, cannot be the case, since the potentials set up with aged electrodes were found to be less positive than those obtained with fresh ones, whereas the former should be richer in the higher oxide. Further, since the E_0' values obtained with massive electrodes of different types fluctuate only within narrow limits, it is difficult to assume the presence of a definite ratio of both oxides. The same observation also excludes the possibility of attributing the shift to concentration polarisation of any type.

(iii) *Effect of the prevailing atmosphere.* Electrodes of the type A_I were examined in atmospheres of hydrogen, nitrogen, and oxygen, and the last, unlike the other two gases, had a profound effect on the electrode (see Fig. 3). This justified regarding the electrode as a metal–metal oxide–oxygen electrode, the potential of which is affected by the prevailing oxygen pressure, so that the cathodic process $O_2 + 2H_2O + 4e = 4OH^-$ is favoured by higher partial pressures. This view is further supported by the fact that the potentials are considerably dependent on temperature. For instance, measurements at 20° and 35° showed a positive shift of *ca.* 100 and 140 mv., respectively, which corresponds satisfactorily to the value of $\Delta E/\Delta t = 2{\cdot}7$ mv./degree often observed in overvoltage phenomena. Since $\Delta E/\Delta t$ for reversible electrodes is usually very small, the effect may be directly ascribed to the absorbed film of oxygen doublets with its movable oxygen atoms which possess volume properties and thus respond to variations in temperature.

(iv) *Effect of cathodic and anodic polarisation.* Massive arsenic electrodes were either cathodically or anodically polarised in 0·1N-sulphuric acid till visible bubbles of hydrogen or oxygen formed on their surface. The results indicated that neither process had a noticeable effect on the electrodic behaviour manifested without polarisation. The rapid formation of a surface oxide film even after cathodic polarisation is the result of the great tendency of the metal to become oxidised and explains satisfactorily why, after immersion, the massive arsenic, in contradistinction from the antimony electrodes (*J.*, 1948, 752, 756), show steady-state potentials not appreciably changing with time. Arsenic differs also from tungsten which, after anodic polarisation, was found not to respond to variations in pH. This may be ascribed to the circumstance that, unlike the latter, the anodic dissolution of the metal is not totally inhibited so that the released metal ions and the hydroxyl ions in the solution form a secondary oxide on the electrode.

Conclusions.—In the light of the above results, the ideas previously developed to interpret the behaviour of the massive antimony electrode may be applied to freshly deposited arsenic electrodes, and these also can be considered as metal–metal oxide–oxygen rather than metal–metal oxide electrodes. In both cases the persistence of oxygen doublets on the electrode surface is imposed by the impermeability of the oxide film to oxygen molecules and by the non-diffusion through it of metal ions towards the solid–gas interface. Although the theory of lattice defects has only been applied to phenomena occurring at about 1000°, when the reactants involved are at "thermodynamic equilibrium," the behaviour of arsenic and antimony, as compared with that of copper when functioning as a metal–metal oxide electrode, provides evidence for the applicability of the theory to oxidation reactions occurring at room temperature and opens new fields of inquiry into the phenomenon of passivation in general.

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