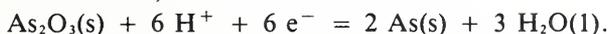


The pH-potential Dependence of the Arsenic Electrode: A Preliminary Study

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Introduction

As a result of his electrochemical investigation of the galvanic couple,
 $\text{Pt} / \text{H}_2(\text{g}) / \text{HClO}_4(\text{m}) // \text{HClO}_4(\text{m}), \text{As}_2\text{O}_3(\text{s}) / \text{As-Pt}$,
Schuhmann (9) reported a standard reduction potential of 0.234 volt at 25°C. for the electrode reaction,



Arsenic behaves as a metalloid and like antimony and bismuth should function as a metal-metal oxide electrode and can be used to measure the pH of a solution potentiometrically. Moussa (7) used the arsenic electrode as the indicator electrode in the potentiometric titration of a dilute solution composed of a mixture of the acids, H_3PO_4 , $\text{HC}_2\text{H}_3\text{O}_2$, and H_3BO_3 , with NaOH. The titration was monitored with the aid of the electrochemical cell,
 $\text{Pt-As} / \text{H}^+ // \text{satd. calomel electrode}$.

From these measurements he reports the reduction potential in volts for the arsenic electrode to be

$$E_{\text{red}} = 0.335 - 0.0597 \text{ pH}$$

at 25°C., valid in the pH range 2.24-11.59. In both researches the arsenic electrodes were prepared by sublimation of the element onto a platinum wire electrode. In this study the electrodes were prepared by the electrodeposition of arsenic onto a base metal from a chloride plating bath.

Procedure

The arsenic electrodes were prepared by electrodeposition onto the base metal from an $\text{HCl-As}_2\text{O}_3$ bath (25 g As_2O_3 per liter of 7 M HCl) recommended by Menzies and Owen (6). The electrodes were plated with arsenic for 15 minutes at a current of 20 milliamperes at room temperature. The anode and cathode compartments were separated by a porous glass frit, a graphite rod served as anode, and the catholyte was stirred during the electrolysis. These conditions produced a bright adherent, metallic plate of elemental arsenic. Platinum wire (surface area 0.5 cm²), platinum foil (surface area 2 cm²), copper wire (surface area 0.8 cm²), and copper wire bent into a spiral (surface area 3 cm²) on which a bright copper deposit was electroplated served as base metal electrodes. The platinum foil electrodes were the most stable. The copper plating bath used is described by Blum and Hogaboom (3). The bath composition is $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ g/l, H_2SO_4 15 g/l, thiourea 0.01 g/l and molasses 0.8 g/l; the plating was done at a current of 80 milliamperes for 20 minutes in a stirred bath with a copper wire anode.

All buffer solutions were prepared in CO_2 -free distilled water from chemically pure reagents. All the reagents were reanalyzed by the methods described by Rosin (8). The pH values for the various buffer solutions were determined electrometrically with the aid of the following galvanic cell



The hydrogen electrode was a Hildebrand-type, and the saturated calomel electrode was a commercial, porous plug-type (Fisher Scientific Company 13-639-52). Six standard buffer solutions recommended by Bates (2) were used to determine the standard reduction poten-

TABLE 1: Primary Standard Buffer Solutions at 25 °C.

Buffer Solution	Molarity	pH
Potassium Tetroxalate	0.04962	1.679
Potassium Dihydrogen Citrate	0.04958	3.76
Acetic Acid	0.0100	4.718
Sodium Acetate	0.0100	
Potassium Dihydrogen Phosphate	0.02490	6.865
Sodium Hydrogen Phosphate	0.02490	
Potassium Dihydrogen Phosphate	0.008665	7.413
Sodium Hydrogen Phosphate	0.03032	
Sodium Tetraborate	0.009971	9.180

tial for the calomel electrode. They are listed in Table 1. Buffer solutions of other pH values were prepared from $\text{HC}_2\text{H}_3\text{O}_2\text{-NaOH}$ mixtures in which the total acetate concentration was 0.02 molar, $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ mixtures in which the total phosphate concentration was 0.05 molal, and $\text{Na}_2\text{B}_4\text{O}_7\text{-HClO}_4$ or $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH}$ mixtures in which the initial tetraborate concentration was 0.02 molal.

All electromotive force measurements were made at a temperature of 25.00 ± 0.05 °C. with an Orion Digital pH Meter (Model 801). A polarographic H-cell with a glass frit served as the electrolysis vessel. Unless otherwise stated, those buffers in contact with the arsenic electrodes were degassed with nitrogen gas for 15 minutes prior to making any potential difference measurements. Even though the data in Tables 2 and 3 are presented in order of increasing pH, the choice of any particular buffer was done in a random fashion.

TABLE 2: E.M.F. Values in Volts for the Cell, Pt / $\text{H}_2(\text{g})$ / buffer / As

pH	Pt-Cu-As foil	Pt-Cu-As wire	Cu-Cu-As spiral	Cu-Cu-As wire
1.679	0.2350	0.2439	0.2432	0.2445
3.530	0.3480	0.3687	0.3556	0.3326
3.776	0.3566	0.4053	0.4053	0.3363
4.032	0.3611	0.3823	0.3790	0.3503
4.044	0.4718	0.4741	0.4727	0.4729
4.351	0.4742	0.4776	0.4760	0.4768
4.718	0.4824	0.4846	0.4826	0.4704
5.102	0.4833	0.4850	0.4864	0.4879
5.410	0.4640	0.4646	0.4775	0.4470
6.280	0.4690	0.4752	(0.5374)	0.4796
6.865	0.4409	(0.5570)	0.4936	0.4562
7.413	0.4749	0.4658	0.4722	0.4596
7.572	0.4709	0.4761	0.4817	0.4818
8.917	0.4684	0.4714	0.4798	0.4757
9.180	0.4489	0.4573	0.5055	0.4656

TABLE 3: E.M.F. Values in Volts for the Cell, As / buffer // satd. calomel electrode

pH	Electrode 1.	Electrode 2.	Electrode 3.	Average
4.051	0.044	0.028	0.053	0.042
4.697	0.057	0.042	0.072	0.057
5.425	0.113	0.112	0.110	0.111
6.248	0.184	0.181	0.181	0.182
6.858	0.217	0.219	0.210	0.215
7.408	0.246	0.249	0.243	0.246
8.167	0.286	0.285	0.269	0.280
8.619	0.307	0.308	0.293	0.302
9.177	0.330	0.333	0.336	0.333

Results and Discussion

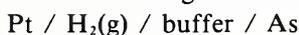
The saturated calomel electrode was calibrated on two separate occasions; separate preparations of the six buffers listed in Table 1 were used. For the galvanic cell,

Pt / H₂(g, p in atm.) / buffer // satd. calomel electrode,
the variation of the electromotive force with pH is of the form

$$E = A + B (\text{pH} + \frac{1}{2} \log p)$$

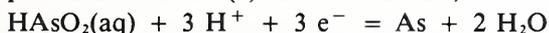
where A corresponds to the reduction potential of the saturated calomel electrode plus the average liquid-junction potential, B is the slope of the curve which is theoretically equal to 0.05915 volt at 25 °C., and p is the pressure of the hydrogen gas over the platinized platinum electrode in atmosphere that served as the hydrogen electrode. Least-squares treatment of the data in both cases gave a value of 0.2431 ± 0.0004 volt for A. In the first calibration the value for B was 0.05898 volt and in the second calibration the value of the slope was 0.05909 volt. In the determination of the value of the pH of the other buffers, the use of the experimentally derived values for A and B translates into an uncertainty of 0.006 pH unit.

If the arsenic electrode behaves as a reversible metal-metal oxide couple, then the electromotive force generated within the galvanic cell,



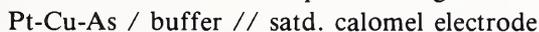
will be constant over that pH range in which there is a unique electrode reaction at the arsenic electrode. Differing values for the electromotive force at differing pH values indicated a different electrode reaction. Table 2 summarizes the potential differences observed for four arsenic electrodes at various pH values. In Table 2, the designation "Pt-Cu-As foil" indicates that the electrode was prepared by the initial plating of copper followed by an arsenic plate onto a platinum foil electrode. The buffer solutions in contact with the arsenic electrodes were purged with nitrogen for 15 minutes prior to the measurements. Measurements of the electromotive force were recorded at 5, 10, and 15 minutes; the 15-min readings are listed in Table 2. The difference between the 5-min and 15-min values was less than 0.005 volt in the majority of cases. At all pH values the oxidation reaction occurred at the hydrogen electrode.

Excluding the first four buffers listed in Table 2, since the electrode reaction is obviously different from that observed in the buffer range, 4.044-5.410 (HC₂H₃O₂-NaC₂H₃O₂ buffers), 6.280-7.572 (KH₂PO₄-Na₂HPO₄ buffers), and 8.917-9.180 (Na₂B₄O₇-HClO₄ buffers) and the two spurious values enclosed in parentheses, the average reduction potential for the four electrodes is calculated as 0.474 ± 0.007 volt. The average of 0.242 volt at a pH of 1.679 approximates the value of 0.247 volt listed in "Standard Potentials in Aqueous Solutions" (1) for the reaction,



The three buffers in the range 3.530-4.032 were formulated from potassium dihydrogen citrate and either perchloric acid or sodium hydroxide. The average value of 0.365 volt over the pH range covered by the citrate buffers might be attributed to an alternate reaction; however, when a potassium hydrogen phthalate buffer of pH 4.008 was used, the potential difference increased to a value above 0.45 volt. Glab (5) reports spurious potential values for the antimony electrode; consequently, a further investigation of the effect of oxalate on the potential of the arsenic electrode at various pH values is under study.

to measure the pH-potential relationship for the electro-deposited arsenic electrode, the potential difference developed in the galvanic cell,



was monitored with three separate electrodes. Three acetate buffers (pH range 4.051-5.425), three phosphate buffers (pH range 6.248-7.409), and three borate buffers (pH range 8.167-9.177) were employed. The buffer solutions were purged with nitrogen gas to remove dissolved oxygen before a potential-difference measurement was made. Preliminary ex-

periments indicated that a relatively stable potential difference was realized after the electrode had been immersed in the buffer for 15 min. In order to eliminate excessive corrosion of the arsenic by the solvent, the electrodes were stored in dry acetone when not in the buffer. The electrodes remained bright during the course of the measurements. The results are compiled in Table 3. In all instances the oxidation reaction occurred at the arsenic electrode.

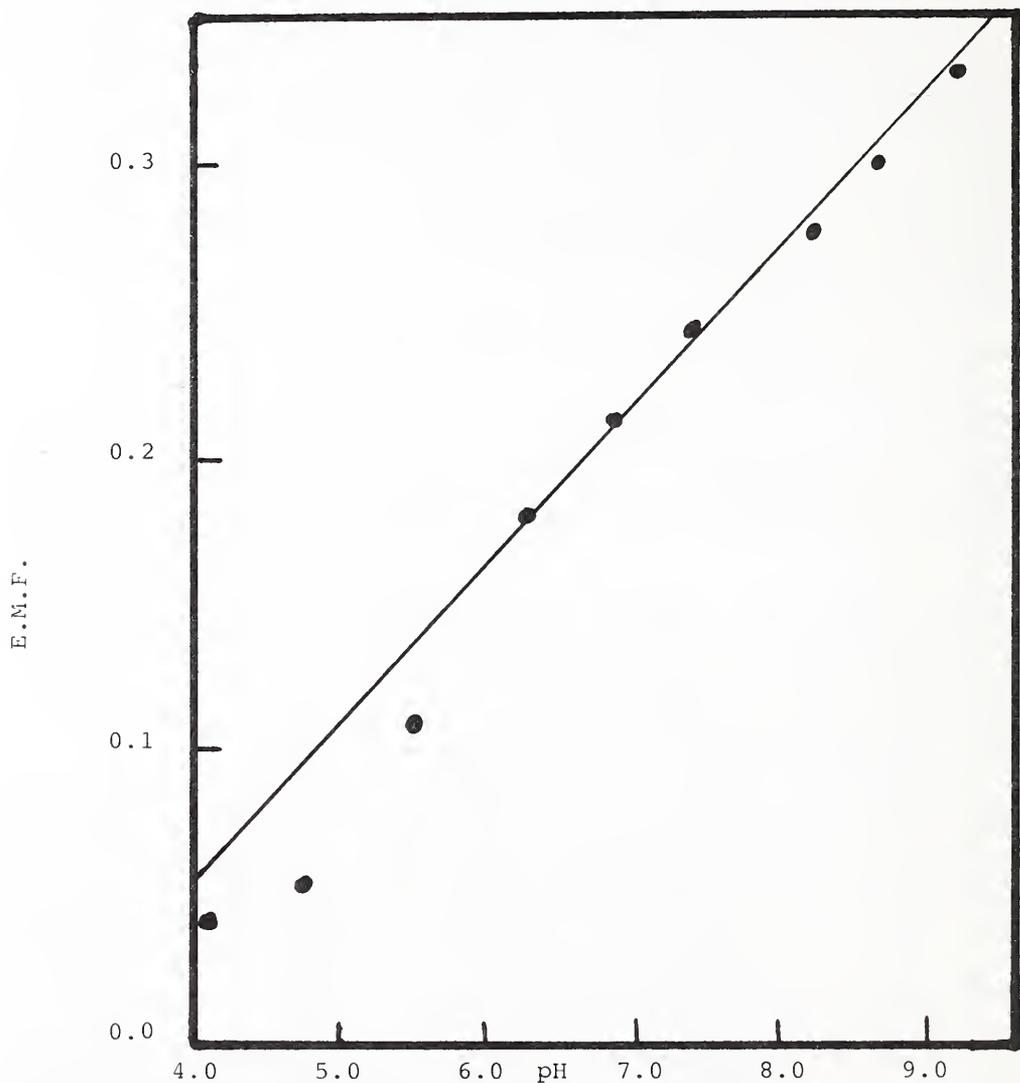


FIGURE 1. The pH-potential behavior for the galvanic cell, As / buffer // satd. calomel electrode, in the range 4.0 to 9.2.

The average potential difference is plotted as a function of pH in Figure 1. A linear relationship is observed over the pH range from 6.2 to 9.2. The least-squares fit to the data in this region yields the relationship in volts

$$E = -0.170 + .0556 \text{ pH}$$

This is the solid line on the graph. In this pH range the reduction potential for the arsenic electrode is calculated in volts as

$$E_{\text{red}} = 0.410 - 0.0556 \text{ pH}$$

In view of the experimental observation that in the cell,



the acetate, phosphate, and borate buffers give similar values for the electromotive force,

no explanation can be given as to why the pH-potential behavior differs among these buffers. A non-Nernstian value of the slope is not surprising since metal-metal oxide electrodes are known to behave irreversibly. In a review of the pH-potential behavior of the antimony electrode Stock (10) summarizes the findings of 25 separate investigations; the reported slopes vary between 0.041 and 0.0647 volt, and in only 5 of the investigations is the theoretical slope of 0.0591 volt listed.

In order to examine the feasibility of using the arsenic electrode as the indicating electrode in potentiometric titrations, approximately 0.1 molar HCl, 0.1 molar $\text{HC}_2\text{H}_3\text{O}_2$, and 0.1 molar HClO_4 were titrated potentiometrically with approximately 0.1 molar NaOH. The base was delivered from a Sargent Constant Rate Buret Model G. The output from the potentiometer during the titration was fed into a recorder, Sargent Model SR, which was driven at a chart speed of one inch per minute. Solutions were stirred but not degassed during the titrations. Separate titrations of the same volume of each acid with the NaOH were monitored with the glass electrode/calomel electrode couple and with the arsenic/calomel electrode couple. The titration curves are reproduced in Figure 2. The behavior of the arsenic electrode during the titration of all of the acids

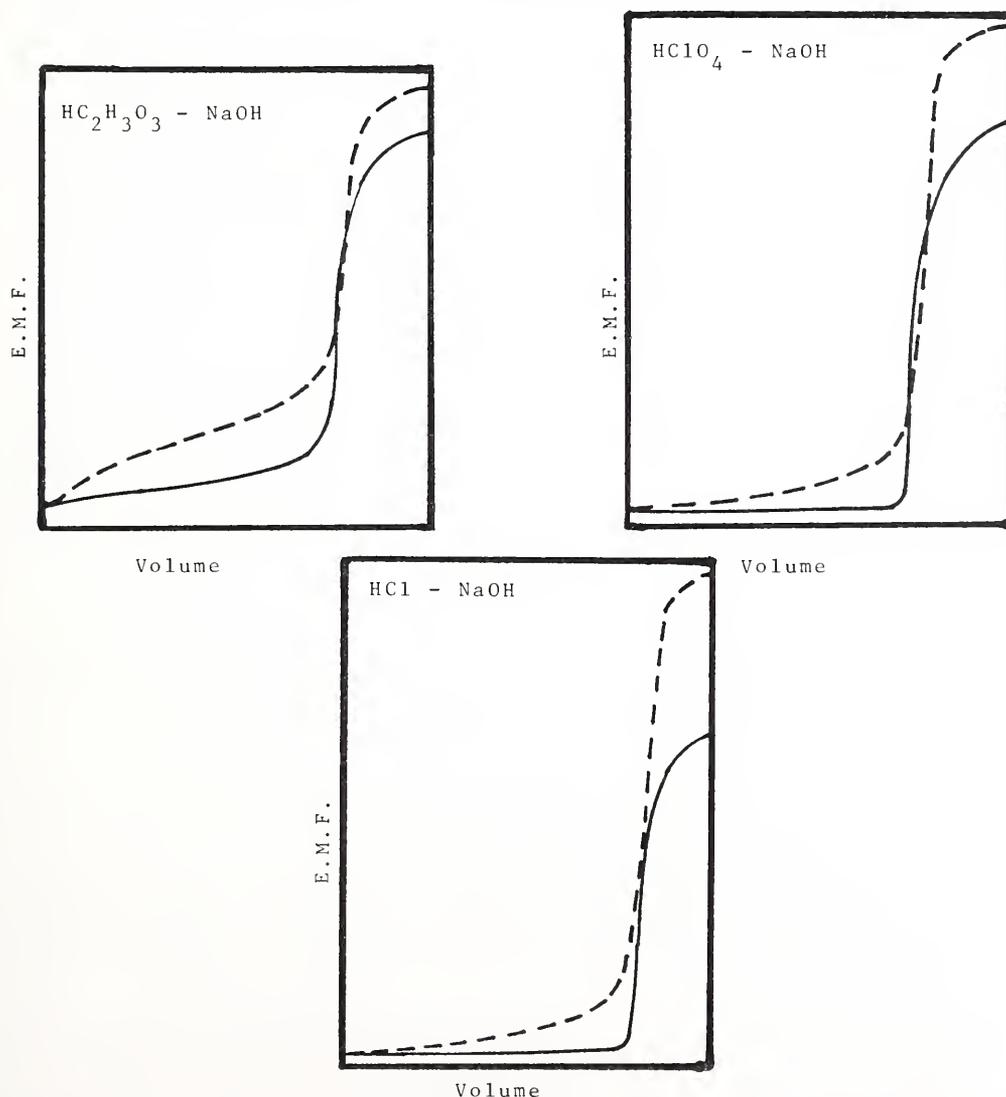


FIGURE 2. Titration curves using the galvanic cells, $\text{As} / \text{H}^+ // \text{satd. calomel electrode}$ (—) and $\text{glass} / \text{H}^+ // \text{satd. calomel electrode}$ (---).

is atypical in that little change in the value of the potential difference is noted until the equivalence point is reached. The volumes of NaOH used to reach the equivalence point with the arsenic and the glass electrodes were HCl (As-20.8 ml, glass-21.4 ml), HClO₄ (As-20.3 ml, glass-21.0 ml), and HC₂H₃O₂ (As-20.8 ml, glass-21.6 ml). The agreement is not good; however, the titrations were done on separate days. Since the difference seems constant, a constant error might be responsible. During an earlier titration study using arsenic plated onto a platinum wire, the results were HCl (As-22.3 ml, glass-22.5 ml) and HC₂H₃O₂ (As-28.2 ml, glass-27.6 ml).

The conclusions reached concerning the behavior of the arsenic electrode are as follows:

1. The potential of electrodeposited arsenic does vary with pH; however, this potential is not a true reversible potential but a corrosion potential. The initial value of the potential at any pH is greater than the potential at the same pH when the electrode is stored in oxygen-free water overnight before the subsequent measurements are made. The potential of different electrodes approached a common value in each buffer after 12 to 24 hours. Similar behavior is reported by Edwall (4) for the antimony electrode.

2. The electrodeposited arsenic electrode is easily prepared and has a fast response to pH change; hence, it should find application as the indicating electrode in titrations in which the glass electrode cannot be used, in particular in certain non-aqueous systems.

3. The presence of dissolved oxygen in any buffer does affect the potential of the arsenic electrode. In a qualitative study we observed that the potential difference between the saturated calomel and arsenic electrodes is less than it is in an oxygen-free buffer. This effect is reversible in that, when the dissolved oxygen is removed with nitrogen, the potential difference increases. The magnitude of the difference seems to depend on pH; however, insufficient data are available to draw a definite conclusion as to whether the effect can be attributable to arsenic behaving as an oxygen electrode.

4. The electromotive force for the cell, As / As₂O₃(s), buffer // satd. calomel electrode, was measured. The electrodes were stored in dry acetone between measurements. The $\Delta E/\Delta pH$ value for the three acetate buffers (pH range 4.02-5.40) was 0.027, for the three phosphate buffers (pH range 6.19-7.36) was 0.038, and for the three borate buffers (pH range 7.71-8.40) was 0.055. The potential difference values in both the phosphate and the borate buffers which were saturated with As₂O₃ were between 0.08 to 0.12 volt less than in the non-saturated buffers of approximately the same pH.

Literature Cited

1. Bard, A. J., Parsons, R., and Jordan, J., editors. Standard Potentials in Aqueous Solution. Marcel Dekker, Inc., New York, 1985, p. 164-72.
2. Bates, R. G. Determination of pH. 2nd. ed. John Wiley and Sons, Inc., New York 1973, p. 59-104.
3. Blum, W. and Hogaboom, G. B. The Principles of Electroplating and Electroforming. 34d. ed. McGraw-Hill Book Company, Inc., New York, 1949, p. 293.
4. Edwall, G., 1979. Influence of Crystallographic Properties on Antimony Electrode Potential—I. Polycrystalline Material, *Electrochimica Acta*, 24: 595-603.
5. Glab, S., Edwall, G., Jongren, P., and Ingman, F., 1981. Effects of Some Complex-forming Ligands on the Potential of Antimony pH-sensors., *Talanta*, 20: 301-11.
6. Menzies, J. A. and Owen, L. W., 1966. The Electrodeposition of Arsenic From Aqueous and Non-aqueous Solutions., *Electrochimica Acta*, 11: 251-64.
7. Moussa, A. A., 1951. The Arsenic Electrode as a pH Indicator. *The Analyst*, 76: 96-103.

8. Rosin, J. Reagent Chemicals and Standards. D. Van Nostrand Company, Inc., New York, 1937.
9. Schuhmann, R. 1924. The Free Energy and Heat Content of Arsenic Trioxide and the Reduction Potential of Arsenic. *J. Am. Chem. Soc.*, 46: 1444-9.
10. Stock, J.T., Purdy, W. C., and Garcia, L. M., 1958. The Antimony—Antimony Oxide Electrode, *Chemical Reviews*, 58: 611-26.

