283. *Studies on Some Metal Electrodes. Part VIII. The Bearing of the Properties of Arsenious Oxide on the Behaviour of the Arsenic Electrode.*

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From solubility measurements in buffers of different pH, arsenious oxide is found to behave as an ampholyte with its isoelectric point at *ca.* pH 4. On one side of that point, the oxide behaves as a monobasic acid with $K_a = 7{\cdot}4 \times 10^{-9}$, and on the other as a mono-acid base with $K_b = 1{\cdot}8 \times 10^{-14}$. In the light of these results the pH–potential plots obtained with different arsenic electrodes, and extending over different ranges of pH according to the type of electrode used, are satisfactorily explained. Owing to the localisation of the isoelectric point and the simpler mode of dissociation in solution of arsenic trioxide, the pH–potential plots obtained with arsenic electrodes of the massive type give slopes coinciding more nearly with the theoretical than do those obtained with massive antimony electrodes.

In the well-known relation connecting the potential of a metal–metal oxide electrode with pH no account is taken of the amphoteric or other properties of the oxide underlying the functioning of the electrode. Deviations from a linear course cannot, therefore, be explained, and it is deemed necessary to plot a calibration relation for any one electrode before utilising it for the measurement of pH. By studying the properties of antimony trioxide in bulk, we were able to interpret the pH–potential curves obtained with the antimony electrode after removal of the oxygen film from its surface, and it was suggested that they represent titration curves of the ortho-base below, and of the meta-acid above its isoelectric point (*J.*, 1948, 759). In this paper, the properties of arsenious oxide in solution are studied by a somewhat different procedure, and it is shown that owing to the position of its isoelectric point and its simpler mode of dissociation as an acid or base, the pH–potential curves obtained with electrodes of different types are satisfactorily explained, and also that, in its massive form, the electrode is better than the antimony electrode for measuring pH.

Experimental.

Preparation of the Octahedral Form of Arsenious Oxide.—The pure oxide (Kahlbaum) was twice recrystallised from pure hydrochloric acid, thoroughly washed with hot water, and repeatedly sublimed in pure nitrogen at *ca.* 195° so as to obtain the octahedral modification stable at room temperature (Smits and Beljaar, *Z. physikal. Chem.*, 1933, **167**, 273). Although the temperature is too low for the oxide to decompose into element and pentoxide, a slight grey residue with pronounced acid properties remained even after the fifth sublimation.

Preparation of the Vitreous Modification.—The above pure product was sublimed in sealed Pyrex flasks at 375—400° (Randall and Doody, *J. Physical Chem.*, 1939, **43**, 613). The protected glassy material could be kept as such for several months without devitrification.

Solubility in Water.—Pure samples of each form were introduced into well-steamed 2-l. saturation vessels of Pyrex glass, each provided with two mercury seals—one for a mechanical stirrer, and the other for an inverted syphon furnished at the ascending end with a sintered-glass disc and ground at the other end so as to fit tightly into a pyknometer. This could be filled with the help of compressed nitrogen passing through a two-way tap sealed at the neck of the flask. The solubility measurements, carried out at 25° and at 35° ± 0·05°, lasted usually for about 50 days, the equilibria being approached both from higher and from lower temperatures, and the rate of stirring being 150—175 r.p.m. Although arsenious oxide sols are not known to exist, the complete settling of the solid usually required 24 hours.

Dissolved As^{+++} was determined potentiometrically with potassium bromate following Györy's procedure as modified by Zintl *et al.* (*Ber.*, 1923, **56**, 472; *Z. anal. Chem.*, 1928, **74**, 330). The inflexion indicating complete oxidation to As^{5+} was sharp and amounted in the average to 400 mv.

Solubility at Various pH.—Samples of the pure octahedral form were introduced, together with about 60 c.c. of a standard buffer of Clark and Lubs's series, into well-steamed flasks of 100 c.c. capacity. These were sealed off, fixed horizontally on a vertical shaft in a water thermostat adjusted at 25° ± 0·05°, and rotated for about 60 days. The pH values of the saturated solutions were then redetermined with the aid of a glass electrode, which was calibrated with buffers whose pH values were accurately determined by means of the hydrogen electrode. The arsenic content of each solution was also determined by the above-mentioned method.

Results.

(i) It was found that saturation of water by the octahedral form is complete after about one month and at 25° and 35° corresponds to 2·0681 and 2·6620 g. per 100 g. of solution, respectively; Anderson and Story (*J. Amer. Chem. Soc.*, 1923, **45**, 1102) give 2·0506 and 2·5636. The solubilities of the vitreous form after the same time are 3·8237 and 3·2975 g. per 100 g. of solution at 25° and 35°, respectively; but these are not equilibrium solubilities since the values tend to decrease with time more quickly at 35° than at 25°, apparently owing to the transformation of the vitreous form *via* the monoclinic into the octahedral one. Similar observations were made by Bussy (*Compt. rend.*, 1847, **24**, 774) and by Winkler (*J. pr. Chem.*, 1847, **24**, 139).

(ii) By plotting the solubility S in the buffers against their original pH values on the one hand and against their pH values at saturation on the other, curves *a* and *b* respectively (Fig. 1) are obtained, showing that S passes through a minimum at about pH 4, which corresponds therefore to the isoelectric point of the trioxide. In Fig. 2 the pH values at saturation are plotted against the original pH, and from this and from the curved line in Fig. 1, it can be seen that the introduction of the oxide affects the pH values of the buffers to an extent increasing with rise of pH. Below pH 7 the effect becomes progressively less marked and all points fall practically on the theoretical line *A* of unit slope. According to Michaelis (*Biochem. Z.*, 1912, **47**, 251), the point of zero Δ pH, which corresponds to the isoelectric point, may be determined by plotting the Δ pH values against the original pH's as shown in Fig. 3. The point of interception of the resulting curve with the straight line *A* of zero slope, although lying in the neighbourhood of pH 4, is not as clearly defined as by the S–pH plots.

FIG. 1.

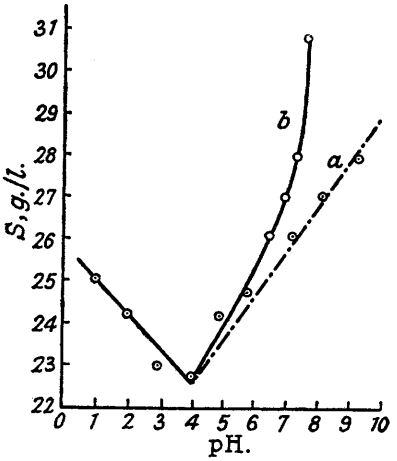


FIG. 2.

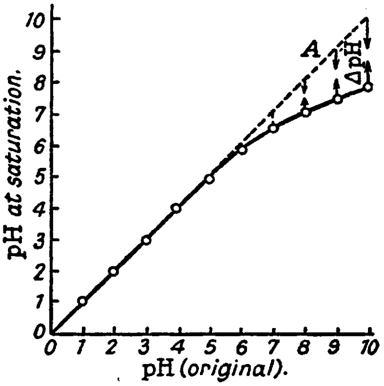
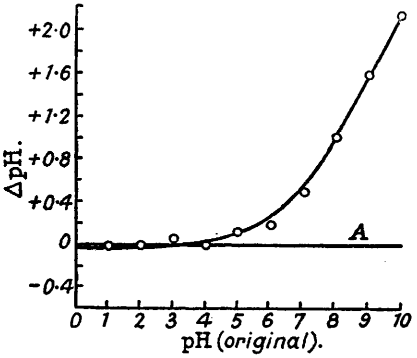


FIG. 3.



In order to evaluate the magnitudes of the acid and basic dissociation constants, use was made of the following relations (Krebs and Speakman, *J.*, 1945, 593) :

$$\log (S/S^\circ - 1) = \mathrm{pH} - \mathrm{p}K_a' \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

and

$$\log (S/S^\circ - 1) = \mathrm{p}K_w - \mathrm{p}K_b' - \mathrm{pH} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

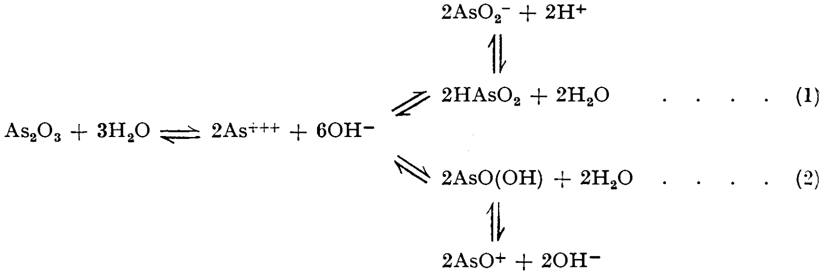
S being the total solubility and S° that in strongly acid solutions; S° may be evaluated by plotting S against $1/[\mathrm{H}^\cdot]$ and extrapolating to $1/[\mathrm{H}^\cdot] = 0$. The values of S at pH 4·49 and 5·80 lead to $S^\circ = 20{\cdot}40$ g./l. The log $(S/S^\circ - 1)$ values are then calculated and found to be as follows :

pH at saturation	1·00	1·99	2·95	3·99	4·88
$1 + \log (S/S^\circ - 1)$	0·342	0·255	0·079	0·041	0·255
pH at saturation	5·80	6·50	7·00	7·38	7·83
$1 + \log (S/S^\circ - 1)$	0·322	0·413	0·505	0·556	0·708

By plotting the $1 + \log (S/S^\circ - 1)$ values against pH at saturation, a curve almost identical with the S–pH plot (curve *b* in Fig. 1) is obtained. By applying equation (1) and using as the most alkaline buffers those with the pH values 7·83 and 7·38, K_a' is found to be $7{\cdot}4 \times 10^{-9}$ and $1{\cdot}5 \times 10^{-8}$, respectively. Equation (2) leads to K_b' values ranging from 22 to $1{\cdot}8 \times 10^{-14}$. The values of K_a' and K_b' are comparable with those obtained by other methods by other authors, which range from 10^{-10} to 10^{-11} for K_a' (Zwadisky, *Ber.*, 1903, **36**, 1435; Wood, *J.*, 1908, **93**, 415) and from 10^{-14} to 10^{-15} for K_b' (Wood, *loc. cit.*; Washburn *et al.*, *J. Amer. Chem. Soc.*, 1913, **35**, 681).

DISCUSSION.

Because arsenious oxide gives an acid solution in water, the reaction $\mathrm{As_2O_3} + \mathrm{H_2O} = 2\mathrm{AsO_2}' + 2\mathrm{H}^+$ has been assumed to occur. Such a representation is, however, too limited, and should be replaced by a set of dynamic equilibria such as :



$$\begin{array}{lll} & 2\mathrm{AsO_2}^- + 2\mathrm{H}^+ & \\ & \Updownarrow & \\ & \nearrow\!\!\!\swarrow\ 2\mathrm{HAsO_2} + 2\mathrm{H_2O} & \quad . \quad . \quad . \quad . \quad (1) \\ \mathrm{As_2O_3} + 3\mathrm{H_2O} \rightleftharpoons 2\mathrm{As}^{+++} + 6\mathrm{OH}^- & & \\ & \searrow\!\!\!\nwarrow\ 2\mathrm{AsO(OH)} + 2\mathrm{H_2O} & \quad . \quad . \quad . \quad . \quad (2) \\ & \Updownarrow & \\ & 2\mathrm{AsO}^+ + 2\mathrm{OH}^- & \end{array}$$

which allows for the existence of As^{+++} ions and thus satisfies the simple relation connecting the potential of a metal–metal oxide electrode and pH. Owing to their amphoteric and other properties, the As^{+++} ions are incapable of existing in appreciable quantity in water. This accounts for the ability of the electrode to function as an indicator electrode for pH in spite of the high solubility of the underlying oxide. The assumption tacitly accepted, that for a metal to function as a metal–metal oxide electrode its oxide should possess very low solubility, appears therefore to be unnecessary.

At the isoelectric zone both reactions indicated by (1) and (2) have equal opportunities to occur and outside that zone, either one may prevail. Considering now reaction (1), it may be noted that $\mathrm{HAsO_2}$ will remain practically undissociated as long as the prevailing pH is lower than its pK_a' value, and any decrease in pH will bring about a corresponding increase in activity of As^{+++} ions. As the pH increases, the acid progressively dissociates until a pH value of the same magnitude as the pK_a' value of the acid is approached, whereupon the acid loses its identity owing to the incidence of the acid–base reaction. Higher pH values are then levelled down owing to the same effect. The same applies *mutatis mutandis* to the reaction represented by (2) in which case the conjugate acid, C_a, of the base AsO(OH) should be considered since all statements are made in terms of pH and not pOH. If the well-known relation $K_{C_a}K_b' = K_w$ is applied and K_w taken as 10^{-14}, K_{C_a} will be approximately unity, and pK_{C_a} zero, and hence any deviations resulting from a base–acid reaction below the isoelectric zone will be negligible above pH = 0.

In the light of these properties of solutions of arsenious oxide, we can now interpret the pH–potential plots given by the different types of arsenic electrode. For instance, polarised electrodes consisting of the freshly prepared massive metal show a linear course over the pH range 3—10 owing to the inability of the oxide on the surface of the metal to level down the buffer above pH 7 or to depolarise the electrode in strongly acid solutions. When the electrodes are used in conjunction with the trioxide, the linear course extends only over the pH range 4—7, the flattening of the curves above that pH being greater with the more soluble vitreous than with the octahedral form of the oxide. Aged electrodes show intermediate behaviour and respond rightly to variations in pH between pH 3 and 8.

Unpolarised electrodes, on the other hand, *i.e.*, electrodes involving the powdered metal, show a linear course between pH 1 and 7 when the trioxide is involved in the electrode systems and this is in harmony with the properties of both electrode and oxide. Otherwise, the relation is not a strictly linear one; the points lying mostly either above or below the theoretical plot on the acid or the alkaline side of pH 7, respectively. It is probable that the mechanism of oxidation of the powdered metal leads to a slight polarisation effect which more or less persists in the absence of appreciable portions of the oxide to saturate the buffers. Out of contact with air the pH–potential plots as based on the final potential values constitute straight lines extending through the approximate pH range 1—7.

A remarkable feature of the pH–potential plots obtained with arsenic electrodes of all types is that, although they extend over different pH ranges according to the type of electrode and for the reasons outlined above, they all manifest a slope, the magnitude of which, in contrast to that of the antimony electrode, coincides closely with the theoretical one. This is apparently connected with the mode of dissociation of arsenious hydroxide simply as a meta-base or acid on both sides of its isoelectric point. Antimony hydroxide was found to behave as an ortho-base below and as a meta-acid above its iso-electric point at *ca.* pH 9 (*loc. cit.*). Although in air the properties of the oxide formed on massive antimony electrodes were masked by the oxygen overvoltage effect, yet owing to its dissociation in steps and to the position of its isoelectric point, the pH–potential plots obtained with such electrodes were found to possess slopes deviating from the theoretical one.

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