The table shows some typical results obtained by this method with samples containing known amounts of iodine. The iodine was added in the form of potassium iodide to samples of mineral mixture containing no iodine or a very slight trace. Blanks were always run on the samples used and on the reagents.

Samples which contain no charcoal or bone meal may be fused with 20 g. of sodium hydroxide alone, omitting the potassium nitrate except for the addition of a few small crystals at the end of the fusion.

Summary

A method is described for the quantitative determination of small amounts of iodine in mixtures of mineral salts, charcoal, spent bone black, etc. The method is a modification of Kendall's and involves fusion with sodium hydroxide and potassium nitrate, removal of interfering substances, oxidation with bromine and determination of the iodine iodimetrically. Necessary conditions are outlined. Other methods were found very unsatisfactory for complex mixtures except when the samples were freshly prepared.

QUINCY, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ANTIMONY-ANTIMONY TRIOXIDE ELECTRODE AND ITS USE AS A MEASURE OF ACIDITY[1]

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Increased realization of the importance of a knowledge of acidity in the control of chemical reactions has aroused a general interest in methods by which the activity of the hydrogen ion may be measured. If we dismiss from consideration the numerous and widely used color indicators, whose applicability rests upon comparative measurements with the hydrogen electrode, the latter at present constitutes by far the most important means of determining acidity. Under strictly defined conditions, it possesses a very high degree of accuracy and reproducibility; the maximum accuracy of the hydrogen electrode is not easy to attain, however, even approximately. The proper functioning of the platinum (or iridium) coating of the electrode is readily affected by traces of many substances not unlikely to be present in the system; reactions catalyzed by the platinum black may affect the hydrogen ion activity of the solution; the necessity of employing a gas phase of known partial pressure of hydrogen is awkward and presents serious difficulties in the investigation of

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[1] From the dissertation presented by E. J. Roberts to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1926–1927.

solutions in equilibrium with a dissolved gas. In this case the gas surrounding the electrode must be such that the equilibrium conditions of the original solution are not disturbed. Solutions containing carbonates, which are of especial interest to the physiological chemist, are but one example of a case in which the gas phase must consist of a mixture of gases of known partial pressure.

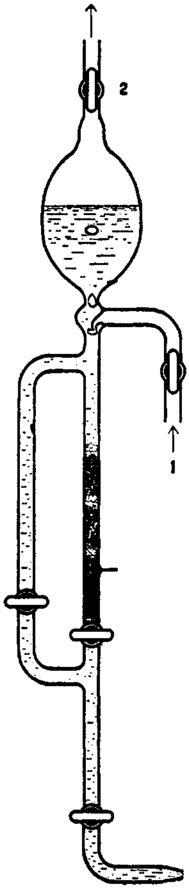

Fig. 1.—Antimony–antimony trioxide electrode for use with nitrogen. 1. Nitrogen inlet. 2. Nitrogen outlet.

The quinhydrone electrode and its several modifications are used quite extensively. The independence of a gas phase is a marked advantage of this electrode but its stability falls far short of that of the hydrogen electrode and it is not usable in solutions of appreciable alkalinity.

Another class of electrodes closely related to the hydrogen in principle but employing no gas phase is the metal oxide electrode, more particularly an electrode made up of a pure metal in contact with a solution saturated with respect to its oxide. Probably the best known example of this type is the mercuric oxide electrode; but, because of the solubility of the oxide, this electrode does not function as a measure of the activity of hydrogen ion except in alkaline solution and in absence of ammonia and of the anions of the slightly soluble mercurous salts, notably the chloride.

The first suggestion for a metal oxide electrode composed of a metal which does not displace hydrogen, whose salts are readily hydrolyzed and whose oxide possesses a low solubility in both acids and bases, was made by Uhl and Kestranek.[3] These authors pointed out that antimony and its amphoteric trivalent oxide meet the requirements over a presumably wide range in acidity. Their working electrode, which was used only as an end-point indicator in acidimetric titrations, was somewhat crude, consisting of a bar of massive antimony standing in the solution in which had been suspended several milligrams of antimony trioxide prepared by treating antimony with nitric acid.

The obvious advantages of such an electrode for measuring acidity led us to make an intensive investigation of the electromotive behavior of antimony and its trivalent oxide. Kolthoff and Hartong[4] have published the results of a brief study of the potential of the antimony–

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[3] Uhl and Kestranek, *Monatsh.*, **44**, 29 (1923).

[4] Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

antimony trioxide electrode in various solutions of known acidity. Their electrode arrangement was that of Uhl and Kestranek; the relation between potential and *P*H was shown to be nearly linear, although the change in potential for each Sørensen unit was always less than that required by theory, diverging more in acid than in alkaline solution. Similar results were obtained in a rather more detailed research by Vlès and Vellinger.[5] After our work was practically complete, Franke and Willaman[6] described a form of antimony electrode for use in the control of pulp and paper manufacture; their electrodes, bars of metal cast with more care than those of previous authors, gave potentials which, at 25°, differed by only 54 mv. for a tenfold ratio of the hydrogen ion activities over the range 1 to 12 *P*H.

In the following we have attempted to define the conditions under which the behavior of the antimony–antimony trioxide electrode approaches the ideal, and also to describe a practical form of the electrode which may be used as a substitute for the hydrogen electrode with no essential decrease in accuracy and a considerably increased field of applicability over the latter. This has involved a study of the condition of both metal and of oxide stable at ordinary temperatures, the effect of oxygen upon the system, the time required for equilibrium to be established and the direction from which it must be approached. Moreover, it has necessitated a detailed examination of the validity of the accepted *P*H values of certain buffer solutions at 25° and, because of the uncertainty of some of the corrections involved, the direct measurement of some of them at 25°.

The Antimony–Antimony Trioxide Electrode at 25°

Corresponding to the electrode reaction $Sb(s) \rightleftharpoons Sb^{+++} + 3\ \ominus$, the potential of an antimony electrode at 25° may be written

$$E_{Sb} = E_0' - (0.05915/3) \log (Sb^{+++}) \qquad (1)$$

In a solution saturated with respect to the trioxide, the following equilibrium may be considered to exist: $Sb_2O_3(s) + 3H_2O \rightleftharpoons 2Sb^{+++} + 6OH^-$, wherefore, substituting in Equation (1) the value for the activity of Sb^{+++}, we have

$$\begin{aligned} E_{Sb} &= E_0 + 0.05915\ [-\log (H^+) - \log (Sb_2O_3)^{1/6} + \log (H_2O)^{1/2}] \\ &= E_0 + 0.05915 \left[P_H - \frac{1}{6} \log (Sb_2O_3) + \frac{1}{2} \log (H_2O)\right] \qquad (2) \end{aligned}$$

Thus, if the last two terms in the equation are disregarded, E_0 is the difference in potential between an antimony–antimony trioxide and a hydrogen electrode in solutions of the same acidity. This cell was measured by Schuhmann[7] in three concentrations of perchloric acid ranging from 0.23 to 1.13 *M*, who demonstrated that in acid solution trivalent

[5] Vlès and Vellinger, *Arch. phys. biol.*, **6**, 38 (1927); Vlès, *ibid.*, **6**, 92 (1927).

[6] Franke and Willaman, *Ind. Eng. Chem.*, **20**, 87 (1928).

[7] Schuhmann, This Journal, **46**, 52 (1924).

antimony is present mainly in the form of SbO^+. The ions Sb^{+++}, $SbOH^{++}$, SbO^+, SbO_2^-, SbO_2OH^{--} and SbO_3^{---} may be regarded as capable of existence under different conditions of acidity. However, provided the system is in equilibrium, Equation (2) is independent of the form of the ion in which the antimony may occur; indeed, it may be very simply derived from the reaction expression $2Sb(s) + 3H_2O \rightleftharpoons Sb_2O_3(s) + 6H^+ + 6\ominus$.

The term in Equation (2) which involves the activity of the solid oxide disappears if the oxide is in its standard state (that is, the stable crystalline form), and this condition must hold if the antimony trioxide electrode is to attain its highest accuracy in acidimetric measurements. Other authors have paid no attention to this point, which has proved to be of major importance.

The term involving the activity of water is not altogether desirable from the standpoint of the applicability of the electrode for determining P_H. It is not always easy to evaluate this term with absolute accuracy but, since the activity of water decreases slowly with increasing concentration of dissolved salts, an approximation can usually be made that is within the experimental accuracy. For instance, even with solutions saturated at 25° with potassium chloride, sodium chloride, and potassium sulfate, respectively, the correction for the activity of water[8] amounts to 2.2, 3.7 and 0.4 mv.; in the case of the buffer solutions used in our experiments this term, being of the order of 0.01 mv., may be entirely neglected.

Since E_0 at 25° for the antimony–antimony trioxide electrode is essentially the potential of the electrode in a solution containing hydrogen ions at unit activity referred to a hydrogen electrode under a partial pressure of hydrogen of 1 atmosphere at 25° in a similar solution, the value of E_0 must be determined by making such a measurement either directly or indirectly, the direct measurement being obviously the more reliable method. However, owing to the fact that previous investigators have found that the coefficient of the second term of the right member of Equation (2) may deviate from theory as much as 10%, the indirect method promised distinct advantages in the study of the electrode under varied, but strictly defined, conditions. Accordingly, if the potential of the antimony electrode in a buffer solution, whose P_H has been determined by means of a hydrogen electrode measurement, is measured against reference electrodes corresponding to those used in the standardization of the buffer, the value for E_0 may be determined provided that (a) the conventions adopted with regard to the liquid junction potentials in the two systems correspond, (b) the reference electrodes in the two cases have the same thermodynamic properties. Since the slope of the E *vs.* P_H curve

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[8] Leopold and Johnston, THIS JOURNAL, **49**, 1974 (1927).

of the antimony electrode is altered by 1 mv. per *P*H (that is, by almost 2%) by a change of as little as 0.12 in the difference attributed to a pair of buffers of *P*H 3 and 10, respectively, and since an uncertainty of this magnitude may easily enter when the buffers are used at a temperature other than that at which the values were set, we were forced to consider very carefully the *P*H of the standard buffers which we used. Furthermore, it is necessary to establish that the liquid junction potentials in our reference system correspond to those used in the standardization of the buffers and to choose the proper potential of our reference electrode.

The *P*H of the Standard Buffer Solutions at 25°

The buffers used in this investigation were those described by Clark and Lubs,[9] the *P*H of which was fixed by means of the hydrogen electrode at 20°, thus rendering a temperature correction to 25° necessary. Table I lists the several buffers with corresponding temperature corrections obtained from a number of sources (Col. 3). In the case of the two potassium chloride-hydrochloric acid buffers, the measurements were made at 25°; the next five were corrected on the basis of the work of Kolthoff and

TABLE I

THE TEMPERATURE CORRECTION AND BJERRUM EXTRAPOLATION FOR THE CLARK AND LUBS BUFFERS

Buffer	C. and L. *P*H at 20°	Temp. corr. to *P*H at 25°	Calcd. *P*H at 25°	Measured *P*H at 25°	Bjerrum, extrapolation, mv.
KCl, HCl	..	...	...	1.2	..
KCl, HCl	..	...	...	2.2	..
KHPhthalate, HCl	2.2	0.008	2.208	....	−0.21
KHPhthalate, HCl	3.0	.008	3.008	3.008	.31
KHPhthalate, NaOH	4.0	.010	4.010	....	.38
KHPhthalate, NaOH	4.4	.010	4.410	....	.43
KHPhthalate, NaOH	5.0	.012	5.012	....	.48
KHPhthalate, NaOH	5.6	.012	5.612	....	.48
KHPhthalate, NaOH	6.0	.013	6.013	6.018	.49
KH_2PO_4, NaOH	6.0	...	6.0	....	.32
KH_2PO_4, NaOH	6.4	...	6.4	....	.36
KH_2PO_4, NaOH	6.6	...	6.6	....	.38
KH_2PO_4, NaOH	7.0	...	7.0	6.975	.41
KH_2PO_4, NaOH	7.4	...	7.4	....	.42
KH_2PO_4, NaOH	8.0	...	8.0	....	.48
H_3BO_3, KCl, NaOH	8.0	−0.02	7.98	7.960	.00
H_3BO_3, KCl, NaOH	9.0	.04	8.96	(8.933)[a]	.05
H_3BO_3, KCl, NaOH	10.0	.06	9.94	9.905	.11
Na_2HPO_4, NaOH	11.29 (18°)	...	...	11.14	..
Na_2HPO_4, NaOH	12.06 (18°)	...	...	(11.91)[b]	..

[a] Interpolated from the preceding and following measurements.

[b] Calculated from direct measurements.

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[9] Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

Tekelenburg[10] on the change of *P*H in buffer mixtures at varying temperatures. Walbaum[11] found the *P*H of the phosphate buffers of the Sørensen series independent of the temperature over a wide interval, therefore the same conclusion was drawn with respect to the similar Clark and Lubs buffers; the corrections adopted for the borate buffers were also taken from Walbaum's work on the Sørensen solutions. The two most alkaline buffers are not from the Clark and Lubs series but were calculated from Ringer's[12] data by Kolthoff. The *P*H at 25° for the supposed *P*H 12.06 buffer is calculated from our own direct measurement on the preceding solution, assuming Kolthoff's difference to be correct. In some instances we determined the *P*H of the buffer directly with a hydrogen electrode; these values, discussed later, are given in the fifth column of the table and are used in subsequent calculations in preference to the computed values (Col. 4), as each of these involves a consideration of the work of more than one author.

Liquid Junction Potentials

Clark and Lubs measured the cells Pt, H_2 | buffer | 1.75 *N* KCl followed by 3.5 *N* KCl | KCl (saturated), Hg_2Cl_2 | Hg and Hg | Hg_2Cl_2, KCl (saturated) | 0.1 *N* KCl, Hg_2Cl_2 | Hg, employing the Bjerrum extrapolation indicated as a correction for the liquid junction potential between the buffer and the saturated potassium chloride, and "neglecting the liquid junction potential between saturated and 0.1 *N* potassium chloride." However, Scatchard[13] showed that in using a flowing junction apparatus in measuring the cell Hg | Hg_2Cl_2, KCl (saturated) || 0.1 *M* KCl, AgCl | Ag[14] the electromotive force did not change on stopping the flow, indicating that the junction potential was independent of the nature of the junction in the case of two potassium chloride solutions, and, therefore, that the combination of liquid junctions 3.5 *N* KCl | KCl (sat.) | 0.1 *N* KCl is exactly equivalent to the junction 3.5 *N* KCl | 0.1 *N* KCl; also that the combination 1.75 *N* KCl | KCl (sat.) | 0.1 *N* KCl is equivalent to 1.75 *N* KCl | 0.1 *N* KCl. This conclusion is still further verified by the fact that Clark found no Bjerrum extrapolation in the measurements on the borate buffers at low sodium ion content, that is, when the ions in the buffers were chiefly potassium and chloride ions. This means that the junction potential 0.1 *N* KCl | 1.75 *N* KCl plus 1.75 *N* KCl | KCl (sat.) equals 0.1 *N* KCl | 3.5 *N* KCl plus 3.5 *N* KCl | KCl (sat.) which may be extrapolated to equal 0.1 *N* KCl | KCl (sat.). Therefore 3.5 *N* KCl | 0.1 *N* KCl equals 3.5 *N* KCl | KCl (sat.) plus KCl (sat.) | 0.1 *N* KCl.

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[10] Kolthoff and Tekelenburg, *Rec. trav. chim.*, **46**, 33 (1927).

[11] Walbaum, *Biochem. Z.*, **107**, 219 (1920).

[12] Ringer, *Verslag. Physiol. Lab. te Utrecht*, **10**, 109 (1909).

[13] Scatchard, THIS JOURNAL, **47**, 696 (1925).

[14] The symbol || indicates a flowing junction.

If this is the case, Clark's liquid junction train is reduced in effect to Bjerrum's original train, solution | 3.5 N KCl followed by 1.75 N KCl | 0.1 N KCl, and the extrapolation tends to reduce the sum of all the liquid junction potentials to zero rather than merely that between the buffer and the saturated potassium chloride solution.

Our measurements were made with the liquid junction system buffer | 3.5 N KCl | 0.1 N KCl; since this corresponds to Bjerrum's train, it, in effect, is equivalent to Clark's train; therefore Clark's determined values for the Bjerrum extrapolation on the several buffers (Table I, last column) may be applied to our readings, thus bringing them into concordance with Clark's corrected potentials. It is to be noted that this correlation of our junction potentials with Clark's and our use of his Bjerrum extrapolations are necessary if we are to use his calculated values for the P_H of the solutions; but it must be emphasized that our derived value for E_0 is independent of any theory of the liquid junction since the corrections applied merely cancel those introduced by Clark in calculating the P_H of the solution.

Potential of Reference Calomel Electrodes

Clark used for the value of the decinormal calomel electrode −0.3385 v. referred to a platinized electrode immersed in a solution normal with respect to hydrogen ions and under an atmosphere of water vapor and pure hydrogen gas at a partial pressure of the latter of 760 mm. at 0°. In order to obtain the value of E_0 for the antimony–antimony trioxide electrode at 25° referred to a hydrogen electrode under 1 atmosphere partial pressure of hydrogen at 25°, now the generally accepted standard, by comparison with a 0.1 M calomel electrode, through the medium of a 3.5 N KCl, silver–silver chloride electrode, it is necessary to correct Clark's value for the 0.1 N calomel electrode for (1) the difference in concentration of hydrogen at a partial pressure of 760 mm. at 0° and 760 mm. at 25°, or 0.89 mv.; (2) the temperature coefficient of the electrode, giving rise to a potential change from 20 to 25° of 0.30 mv.;[15] (3) the difference in concentration between 0.1 N and 0.1 M potassium chloride, or −0.15 mv. The resulting value, -0.3374_6 v., refers our measurements to the desired hydrogen standard and to Clark's P_H scale, which, in turn, depends upon the absolute accuracy of his adopted value and his liquid junction corrections. The validity of the scale comes into question later when 0.1 M and 0.01 M hydrochloric acid solutions were used in some of the electrodes and the P_H values calculated on the basis of Scatchard's[13] values for the activity coefficients of hydrogen ion.

On the basis of the activity coefficients for hydrochloric acid[16] from

[15] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, **1925**, Chap. XIX.

[16] Scatchard, THIS JOURNAL, **47**, 641 (1925).

which those for hydrogen ion were derived, Scatchard finds the absolute value of the 0.1 *M* calomel electrode, including no junction potentials, to be −0.3353 v.[13] This calculation, however, is based on the value 0.3989 v. (average of best existing values in the literature, as judged by Scatchard) for the electromotive force of the cell Pt, H_2 | 0.1 *M* HCl, Hg_2Cl_2 | Hg which leads to 0.0466 v. for the difference between the calomel and the silver–silver chloride electrodes. In view of the fact that our direct measurements of this potential[17] using 0.1 *M* potassium chloride gave 0.04530 v. ± 0.05 mv. and that the calomel electrode is known to behave erratically in dilute hydrochloric acid solutions, we prefer to calculate the value of the calomel from Scatchard's measurements of the cell Pt, H_2 | HCl, AgCl | Ag[16] and our own value[18] for the difference between the silver chloride and calomel electrodes. Calculation of Scatchard's results to exactly 0.1 *M* hydrochloric acid gives 0.35230 v.; adding our value of 0.04535 v. we arrive at a result of 0.39765 v. for the potential of the hydrogen–calomel cell in 0.1 *M* hydrochloric acid. A value almost identical with this may be calculated from measurements presented later in Tables IV and V; that is, the electromotive force of the cell Pt, H_2 | 0.1 *M* HCl, Sb_2O_3 | Sb is 0.14436 v.; that of the cell Sb | Sb_2O_3, 0.1 *M* HCl || 3.5 *N* KCl, AgCl | Ag is 0.1259 v.; and for the cell Ag | AgCl, 3.5 *N* KCl || 0.1 *M* KCl, Hg_2Cl_2 | Hg the electromotive force is 0.13135 v.; from this it is evident that the electromotive force of the combination Pt, H_2 | 0.1 *M* HCl || 3.5 *N* KCl || 0.1 *M* KCl, Hg_2Cl_2 | Hg is 0.4016 v. In a paper to be published shortly, we will show that the difference between the two flowing liquid junction potentials indicated is 3.9 mv., which gives 0.3977 v. for the electromotive force of the cell Pt, H_2 | 0.1 *M* HCl, Hg_2Cl_2 | Hg if the activity of chloride ion in 0.1 *M* HCl and 0.1 *M* KCl is the same. Both of these values lead to an E_0 for the electrode Hg | Hg_2Cl_2, Cl^- of −0.2680 v., and −0.3341 v. for the potential of the decimolal calomel electrode, using Scatchard's values for the necessary activity coefficients.[19]

Thus, since the correct value for the potential of the decimolal calomel

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[17] Roberts and Fenwick, THIS JOURNAL, **49**, 2787 (1927).

[18] In view of later measurements in connection with liquid junction potentials soon to be published, the highest of the possibilities indicated above, 0.04535 v., is judged to be more nearly accurate.

[19] Randall and Young, in a paper appearing just after the writing of this paper had been completed, THIS JOURNAL, **50**, 989 (1928), give the following values:

	Randall and Young	Our values
Pt, H_2 | 0.1 *M* HCl, Hg_2Cl_2 | Hg, *E*	0.3976 v. (p. 990) 0.3977 v. (p. 993)	0.3977 v.
Hg | Hg_2Cl_2, Cl^-, E_0	−0.2676 v.	−0.2680 v.
Hg | Hg_2Cl_2, 0.1 *M* KCl, *E*	−0.3341 v.	−0.3341 v.

The agreement between the two sets of results is remarkable, the difference in the second value in the two cases being due to the use of different activity coefficients in the calculations.

electrode, corresponding to Scatchard's activity coefficients of hydrogen ion, is -0.3341 v., and we are using -0.3374_6 v., we must either make a special case of the two hydrochloric acid solutions and use -0.3341 v. for the potential of this cell in our calculations in these two instances, or else modify the calculated *P*H by an amount equivalent to the difference between the two calomel values, this being 3.3_6 mv. (0.3374_6–0.3341) or 0.0568 *P*H, which must be subtracted from the given calculated values (1.075 and 2.036) in order to make them conform to Clark's scale and our own working value for the calomel electrode; these computed values for 0.1 *M* and 0.01 *M* hydrochloric acid solutions become 1.018 and 1.979 *P*H, respectively, upon applying the above adjustment.

From this it is clear that our value for the E_0 of the antimony–antimony trioxide electrode is independent of any *P*H scale, since in both cases we have in effect used a value for our reference electrode which corresponds to that of the author from whose work the *P*H of our solution was derived. The absolute value of the hydrogen ion activity, as derived from measurements with this type of electrode as well as the hydrogen electrode, depends, of course, upon the value attributed to the reference electrode. For this the value -0.3341 v. for the potential of the 0.1 *M* calomel seems to be preferable, while if the relative activity of hydrogen ion is desired, the value -0.3374_6 v., corresponding to that used by Clark, may be used as this leads to results in concordance with the generally accepted *P*H scale.

Preparation of Solutions and Materials

Buffer Solutions.—The standard buffer solutions were made up much as directed by Clark;[20] potassium chloride, potassium acid phthalate, potassium dihydrogen phosphate and boric acid were recrystallized as advised but the buffers were prepared as needed from weighed samples of the salts rather than from stock solutions. A special grade of disodium hydrogen phosphate ($Na_2HPO_4{\cdot}2H_2O$) was purchased ready for use.[21] A solution of constant boiling hydrochloric acid, analyzed gravimetrically, was used in the most acid buffers, and for the standardization of carbonate-free sodium hydroxide obtained by diluting a stronger hydroxide solution prepared by dropping metallic sodium into a deep ether layer above water.[22] All of the water used for the solutions was freshly distilled and collected in a current of escaping steam.

Antimony.—Pure crystalline antimony was prepared by the rapid electrolysis of antimony trifluoride solution, as described by Schuhmann;[7] however, the product was not allowed to dry but was kept under water until needed, treated with hot, dilute hydrofluoric acid and washed. The trifluoride solution was obtained by dissolving specially purified precipitated oxide in pure hydrofluoric acid.

Antimony Trioxide.—The oxide required for the antimony electrode was obtained from the hydrolysis of antimony trichloride, which was prepared in a very high state

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[20] Clark, ref. 15, Chap. VI.

[21] From LaMotte Chemical Products Co., Baltimore, Md.

[22] Cornog, THIS JOURNAL, **43**, 2573 (1921). The sodium carbonate content of our solution was shown by nephelometric comparison to be less than 0.01% of the sodium hydroxide present; no cloudiness developed on the addition of barium chloride.

of purity by distilling the hydrochloric acid solution of commercial "c. p." antimony trioxide[23] in an all-Pyrex apparatus. The high boiling point of antimony trichloride (above 220°) renders an elaborate still unnecessary; a 1-liter distilling flask with the neck drawn down to about 8 mm. in diameter, stoppered with a flanged rod and a 70–80-cm. length of tubing slipped over the side arm for a condenser serves excellently. The distillate was discarded until a test drop of the dense, highly refractive liquid solidified on striking a cold glass surface. The collected product was melted, poured into about 15 times its volume of water and allowed to stand overnight at 80°. The initial voluminous flocculent precipitate of basic chloride became coarsely crystalline; it was washed with distilled water, digested twice for eighteen hour periods at 80° with a strong solution of carefully recrystallized sodium carbonate and then with hot distilled water for three weeks, the water being changed daily. The resulting very finely divided oxide, which will be termed "precipitated oxide," was filtered and dried at 110°; it was easily and completely soluble in hydrochloric acid and gave no chemical test for pentavalent antimony.

Consideration of the behavior of the electrodes containing this precipitated oxide as a solid phase (Nos. 1 and 2) led us to undertake a study of the allotropy of antimony trioxide with the view of obtaining definitely stable, crystalline material.

The Allotropic Forms and Transition Temperature of Antimony Trioxide

A cubic form of antimony trioxide occurs naturally as Senarmontite, and an orthorhombic form as Valentinite. The literature with regard to the form stable at 25° is indefinite.

Small amounts of our pure precipitated oxide were placed in a platinum boat in a sealed, evacuated Pyrex tube, heated in a small electric furnace, cooled quickly and the products examined under a petrographic microscope. A platinum–platinum-rhodium thermocouple with direct reading galvanometer, calibrated at the sulfur point, was used to measure the temperature of the furnace. A sample heated at 550° for twelve hours gave as a product cubic crystals only, 0.005 mm. to 0.02 mm. in diameter, octahedra and octahedra truncated by the cube, dodecahedron, or both. A sample heated at 590° for twelve hours gave orthorhombic crystals only; the orthorhombic form also separates from the molten material when it is allowed to crystallize. On heating these orthorhombic crystals at 550° for twenty-four hours, no trace of the original crystal form remained, transformation to the cubic being complete. At 380° no crystallization of the original oxide took place in twenty-four hours, while at 470° cubic crystals were formed from all samples in twenty-four hours. This was chosen as a safe temperature at which to heat the oxide for future use in the electrodes.

The transition point of antimony trioxide, which must lie between 550 and 590°, was found by a series of successive trials. A final run was made

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[23] Every sample of antimony trioxide that we were able to procure contained considerable quantities of sulfide, which made drastic methods of purification an obvious necessity.

at 573°, as recorded when the thermocouple extended to within 2 cm. of the front of the platinum boat, which did not rest on the bottom of the furnace. At the end of six hours the tube was removed and allowed to cool. The material in the boat was found to consist of orthorhombic crystals only in the rear end, a mixture of orthorhombic and cubic in the middle section and cubic crystals only for the first centimeter. The temperature gradient of the furnace, although not extreme, was positive toward the rear, therefore 570 ± 10° was adopted as the temperature at which cubic and orthorhombic crystals of antimony trioxide are in equilibrium under the pressure of their own vapor, the cubic being the stable form below this temperature.

In order to ascertain the structure of the unheated precipitated oxide, powder photographs were taken of this material, a similar product obtained by treating antimony trichloride over a period of months with water only and which showed a positive orthorhombic structure under the microscope,[24] cubic crystals prepared by heating at 525°, and orthorhombic crystals prepared by sublimation at 600°. The lines from the water hydrolyzed material checked the lines of the orthorhombic control perfectly, while the lines from our oxide prepared by sodium carbonate hydrolysis differed from the orthorhombic control only in that the principal line was broader, extending from 3.14 Å. to 3.21 Å. The principal line of the orthorhombic is 3.13–3.15 Å., of the cubic 3.22 Å., indicating that our precipitated oxide consisted of a mixture of both crystal forms with the orthorhombic greatly predominating.

Preparation of Electrodes and Method of Measurement

Antimony–Antimony Trioxide Electrode.—The electrode vessel used was a modification of the type described by Brönsted[25] in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, to the junction. The modified vessel and the mica-plate flowing junction arrangement have been discussed in an earlier paper.[17] The addition of the by-pass so that there is no flow of electrolyte past the electrode metal while the potentials are being measured is of the utmost importance in this work. In setting up an electrode, the vessel was first filled with water to prevent the entrainment of air bubbles and the main arm was then packed with antimony crystals (or a mixture of metal and oxide) using cotton plugs to prevent clogging of the stopcock and to break the column into several sections. This insures a sufficiently rapid flow of electrolyte for thorough washing when the solution is being changed and also assists in equilibrating the flowing solution with metal or metal and oxide before it reaches the electrode proper.

Hydrogen Electrode.—The hydrogen electrode vessel adopted was of the type described by Lewis, Brighton and Sebastian.[26] The electrode consisted of a section of

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[24] This material was very kindly supplied by Mr. J. E. Cavelti, Wesleyan University, together with many valuable suggestions with regard to the preparation of pure antimony trioxide.

[25] Brönsted, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **3**, No. 9 (1920).

[26] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

gold plated platinum foil coated with a thin layer of platinum black. Tank hydrogen was purified for use by passing through a strong solution of sodium hydroxide, over phosphorus pentoxide and through two 75-watt tungsten filament bulbs before entering the presaturator.[27]

Reference Electrodes.—The antimony–antimony trioxide and hydrogen electrodes were measured against a silver–silver chloride electrode in 3.5 N potassium chloride[28] as a reference; this in turn was checked against a decimolal calomel electrode as the ultimate standard. The silver and calomel electrodes were made up as outlined in the former investigation[17] except that the mercury for the calomel electrodes was even more carefully purified. After spraying many times through dilute nitric acid, it was distilled several times under diminished pressure in air as described by Hulett,[29] followed by a double distillation *in vacuo*.[30]

The electrode system was maintained at 25 ± 0.02° in an air thermostat. A Leeds and Northrup Type K potentiometer was used and the working standard Weston cell was checked at frequent intervals against two newly calibrated cells purchased from well-known makers.

The Measured Electromotive Force of the Cell Sb | Sb_2O_3, Solution || 3.5 N KCl, AgCl | Ag at 25°

A. Precipitated Oxide, Air Substantially Excluded (Electrodes Nos. 1 and 2).—The first measurements of the potential of the antimony–antimony trioxide electrode were made with precipitated oxide. In the preparation of duplicate electrodes (Nos. 1 and 2 of Col. 2, Table II), the platinum lead-wires were given a very thin electroplate of antimony from a trifluoride solution and the columns filled with antimony alone, the only oxide introduced being that suspended in the saturated solutions. Each electrode solution was saturated with the respective soluble constituents of the electrode by shaking in the thermostat with an excess of the solids over a period of at least twelve hours. In the case of the solutions for the antimony electrodes, both oxide and metal were used, the metal being introduced to reduce any pentavalent antimony that might be present. The equilibrating solutions completely filled the containing bottles to avoid the presence of air; after equilibration, they were siphoned quickly into the electrode vessels until the bulb was completely filled and an Orsat bulb containing hydrogen was connected to the top. Immediately before the introduction of the equilibrated solution, the electrodes were thoroughly washed with a similar unequilibrated solution and, immediately after, thoroughly washed again. Readings were taken at various intervals over a period of from seventy-two to ninety-six hours, at the end of which time the next solution was intro-

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[27] Clark, ref. 15, Chap. XV.

[28] The electrode solution contained 3.5 moles (air weight) of potassium chloride per liter at 20°; $d_4^{20} = 1.1526_5$, or the solution was 3.927 molal (vacuum weight).

[29] Hulett, *Phys. Rev.*, **33**, 307 (1911).

[30] The additional precautions were evidently unnecessary since the electromotive force found for the cell Ag | AgCl, 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg checked our former result precisely.

duced. The metal was rinsed with fresh solution from the reservoir bulb after every reading during the first forty-eight hours and occasionally during the rest of the run. The potential difference showed an upward trend with time, the increase during the first twenty-four hours after the introduction of a new solution normally amounting to from 3 to 6 mv., disregarding erratic changes during the first hour or so. After twenty-four hours, further change was very slow. For example, after the first forty-eight hours, the potential with the buffer of *P*H 1.2 remained constant to within 0.5 mv. for forty-eight hours, at the end of which the experiment was closed. The deviations during this period showed no definite trend.

The observed potentials given in the third column of Table II were read at least twenty-four hours after setting up the cell. The fourth column contains the observed potential difference corrected for the liquid junction potential by means of the Bjerrum extrapolation given in the last column of Table I. These values were plotted against the corrected *P*H of the buffers (Col. 1) and a straight line with slope 0.05915 was drawn through the points. The line fitted the data within the limit of experimental accuracy from *P*H 5 to *P*H 10. The rate of change of potential with *P*H thus being fixed, E_0 was calculated from the equation E_0 =

TABLE II

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL Sb | Sb_2O_3, SOLUTION || 3.5 *N* KCl, AgCl | Ag AT 25° (ELECTRODES NOS. 1 AND 2)

*P*H of soln.	Elect. Nos.	E (obs.), volts	E' (E corr. for j.p.), volts	E_{Sb} ($E' - 0.2061$), volts	E'' (0.05915 *P*H), volts	E_0 ($E_{Sb} - E''$), volts	Dev. from $E_0 = -0.1512$ millivolts
1.2	1	0.1331	....	−0.0730	0.0710	−0.1440	...
2.2	1	.1954	....	−0.0107	.1301	.1408	...
3.008	1	.2315	0.2312	+0.0251	.1779	.1528	...
4.010	2	.2978	.2974	.0913	.2372	.1459	...
5.012	1	.3531	.3526	.1465	.2965	.1500	−1.2
5.612	2	.3892	.3887	.1826	.3319	.1493	−1.9
6.0	1	.4090	.4087	.2026	.3549	.1523	+1.1
6.0	1	.4070	.4067	.2006	.3549	.1543	+3.1
6.0	2	.4072	.4069	.2008	.3549	.1541	+2.9
6.4	1	.4309	.4305	.2244	.3786	.1542	+3.0
6.4	2	.4335	.4331	.2270	.3786	.1516	+0.4
6.6	2	.4471	.4467	.2406	.3904	.1498	−1.4
6.975	2	.4705	.4701	.2640	.4126	.1486	−2.6
7.4	1	.4930	.4926	.2865	.4377	.1512	0.0
8.0	2	.5298	.5293	.3232	.4732	.1500	−1.2
7.960	1	.5250	.5250	.3189	.4708	.1519	+0.7
8.933	2	.5849	.5848	.3787	.5284	.1497	−1.5
9.905	1	.6418	.6417	.4356	.5859	.1503	−0.9
11.14	2	.7161	.7161	.5100	.6589	.1489	...
11.91	1	.7656	.7656	.5595	.7045	.1450	...
				Mean (*P*H 5 − *P*H 10)		− .1512	1.6

E_{Sb} − 0.05915 P_H (Equation (2) rewritten on the basis of our stated assumptions), where E_{Sb} is the potential of the antimony–antimony trioxide electrode alone, obtained by adding to E' the value for the potential of the reference half cell, −0.2061 v. This was derived from our measured electromotive force of the cell Ag | AgCl, 3.5 N KCl || 0.1 M KCl, Hg_2Cl_2 | Hg, 0.13135 v., and the value for the decimolal electrode at 25° corresponding to that employed by Clark and Lubs in the standardization of their buffer solutions, −0.3374$_6$ v. The mean value of E_0 over the range in P_H stated was −0.1512 v., with a maximum deviation of 3.1 mv. and a mean deviation of 1.6 mv.; below P_H 5 and above P_H 10, the deviation was greater. If the computed values of P_H (Col. 4, Table I) were used to the exclusion of any of our later determined values, the slope was less than the theoretical, about 0.0586. Schuhmann[7] found 0.1524 v. for the electromotive force of the cell Pt, H_2 | $HClO_4$, aq., Sb_2O_3 | Sb with a maximum deviation from the mean of his three cells of 2.5 mv., a result which compares favorably with our own.

Thus far the antimony–antimony trioxide electrode had exhibited two distinct peculiarities; the "best" E *vs.* P_H curve is not linear except from P_H 5 to P_H 10, the slope, based on the most reliable published values for the buffers, tending to be rather less than the theoretical, and the approach to a constant potential being very slow, sometimes requiring days. In the case of our measurements the first abnormality is not large, but it is in the same direction as the much larger deviations found by other workers.[4,6] Several explanations for the erratic behavior of the electrode suggest themselves. (1) The assumption that the term in Equation (2) involving the activity of the solid oxide drops out may not be valid because the oxide used was not in its stable state and a virtual supersaturation of the solution with antimony trioxide persisted. This would not only explain the slow change of the potential with time but it is a plausible reason for the departure of the curve from linearity and from the ideal slope, since it is easy to believe that the rate of approach to equilibrium might always be slow and yet vary considerably with the acidity. (2) Extreme precautions to exclude air were not taken. It is possible that the system is more susceptible to oxidation than supposed, pentavalent antimony ions forming so readily that the equilibrium $Sb^{+++++} + Sb \rightleftharpoons Sb^{+++}$ is attained with difficulty.[31] (3) The derived P_H values assigned to the buffer solutions may not be actually correct. Although suspicion of the accuracy of the temperature corrections employed for the buffers is justifiable, this last reason for inconsistency will, for the present, be disregarded; in view of the facts that two crystal forms of antimony trioxide are known and the material used showed no definite crystal structure at a magnifi-

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[31] Franke and Willaman report serious drifts in potential on bubbling air through their solutions.

cation of 1000 diameters, the first explanation seemed most likely. Consequently the study of the allotropy of antimony trioxide was made and a supply of definitely pure cubic oxide prepared.

B. Cubic Oxide, Air not **Excluded (Electrodes Nos. 3 and 4).**—Two new electrodes were made up with cubic antimony trioxide in order to investigate its electromotive behavior and to compare it with the precipitated oxide in electrodes Nos. 1 and 2. In keeping with the precautions with regard to the exclusion of any unstable oxide, the subject of the constant activity of the metal was considered. Although the presence of a large number of unstrained crystals of metal in contact with strained metal is supposed to dissipate the strain, electroplating of the platinum lead-wire was discontinued. Instead, it was pretreated with a strong solution of stannous chloride in hydrochloric acid, washed, and a solution of antimony trifluoride introduced to adjust the potential of the wire to that of antimony,[32] before the electrode column was filled, in this case with an intimate mixture of metal and oxide. Crystals of antimony prepared as described for the first two electrodes were used in electrode No. 3; for No. 4 the metal was annealed by heating to 500° in a vacuum, followed by slow cooling. Before use, the annealed metal was treated with boiling hydrofluoric acid for several minutes and washed thoroughly. No precautions were taken to exclude air beyond a soda-lime guard tube in the top of each electrode to avoid the absorption of carbon dioxide, and the solutions were unequilibrated with either metal or oxide before their introduction into the electrode reservoirs.

The pair of electrodes was read over a period of from forty-eight to ninety-six hours after introduction of the buffers. In most cases, the final value was reached within fifteen or twenty-four hours, the potential thereafter remaining constant within 0.2 mv. or less. Upon rinsing the metal with fresh solution from the bulb, a drop of 2 to 3 mv. occurred; after a lapse of ten hours, the electrode had always returned to constant potential. In all cases in which the change of potential with time at the beginning of an experiment was studied, the readings at the end of the first thirty minutes were never more than 6 mv. lower than the final value. Table III shows the behavior of these electrodes. The column headings are self-explanatory and the calculated values given in the table were arrived at in a manner similar to those in Table II, except for Col. 6, in which the value 0.05835 for the slope was determined analytically on the basis of the values for electrode No. 3. The average value for E_0 was also based on the values for electrode No. 3, excluding the widely divergent value at P_H 6.018. The final column indicates the direction

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[32] A similar procedure was found of great value in the preparation of noble metal electrodes for use in the electrometric determination of silver by precipitation as silver chloride, Van Name and Fenwick, THIS JOURNAL, **47**, 9 (1925).

of approach to equilibrium, that is, whether the preceding solution in the electrode had been more alkaline or more acid; *U* signifies that this solution had been more acid and *D* the reverse. It will be noticed that electrode No. 3 is the more consistent of the two, the mean deviation being but 0.17 mv. if the value at *P*H 6.018 is excluded, and that in this case the equilibrium was always approached from the more alkaline side; this peculiarity was also noticed in later work. The values for E_0 for electrode No. 4 are in general more negative than those for No. 3 (the mean being −0.1513 v.), indicating greater mobility and therefore less strain; nevertheless, no significance was attached to the fact that the metal was annealed, since the individual deviations from the mean are considerably greater than for No. 3, and since later work showed that approach to equilibrium from the acid side, as was the case with No. 4, always tended to give slightly low and varying readings.

Table III

The Measured Electromotive Force of the Cell Sb | Sb_2O_3, Solution || 3.5 *N* KCl, AgCl | Ag at 25° (Electrodes Nos. 3 and 4)

*P*H of soln.	Elect. Nos.	*E* (obs.), v.	*E'* (*E* corr. for j.p.), v.	E_{Sb} (E' − 0.2061), v.	*E''* (0.05835 *P*H), v.	E_0 (E_{Sb} − E''), v.	Dev. from E_0 = 0.1504, mv.	Dir. of app. to equilib.
2.2	3	0.1846	0.1844	−0.0217	0.1284	−0.1501	−0.3	D
2.2	4	.1832	.1830	−0.0231	.1284	.1515	+1.1	U
3.008	3	.2315	.2312	+0.0251	.1755	.1504	+0.0	D
3.008	4	.2322	.2319	.0258	.1755	.1497	−0.7	U
4.01	4	.2868	.2864	.0803	.2340	.1537	+3.3	D
4.41	4	.3148	.3144	.1083	.2573	.1490	−1.4	U
6.018	3	.4047	.4042	.1981	.3502	.1521	+1.7	D
6.018	4	.4025	.4020	.1959	.3502	.1543	+3.9	U
6.975	3	.4630	.4626	.2565	.4070	.1505	+0.1	D
6.975	4	.4589	.4585	.2524	.4070	.1546	+4.2	U
7.960	3	.5200	.5200	.3139	.4645	.1506	+0.2	D
7.960	4	.5188	.5188	.3127	.4645	.1518	+1.4	U
8.933	3	.5770	.5769	.3708	.5213	.1505	+0.1	D
8.933	4	.5815	.5814	.3753	.5213	.1460	−4.4	U
9.905	3	.6341	.6340	.4279	.5780	.1501	−0.3	D
					Mean (No. 3)	−0.1504		

The use of cubic instead of precipitated oxide, therefore, resulted in smaller deviations from a straight line relationship between the potential and *P*H, over a wider range in *P*H (2.2–10); but the slope of the straight line was now further from the theoretical than before. Hence only a part of the abnormal behavior of the electrodes could be ascribed to the presence of an unstable solid phase and the effect of complete elimination of dissolved oxygen from the electrolyte was next investigated.

C. **Cubic Oxide, Air Completely Eliminated (Electrodes Nos. 3a, 4a and 5)**.—New reservoir bulbs of 150-cc. capacity were sealed onto electrodes Nos. 3 and 4 without disturbing the metal and oxide, making the completed electrodes (Nos. 3a and 4a) appear as shown in the figure. The electrolyte was drawn up into the bulb through the nitrogen inlet tube by applying suction at the outlet tube. After washing the entire electrode thoroughly with the unequilibrated solution, the bulb was filled, a rubber tube, connected to a nitrogen supply,[33] was attached to the inlet tube and nitrogen bubbled through the solution for three or four hours; the solution in the by-pass was displaced by the oxygen-free solution, and the metal was then washed slowly with the deoxygenated solution for ten to twenty minutes. After twelve hours the nitrogen was again started; an hour later a reading was taken and the metal again washed. Twelve

Table IV

The Measured Electromotive Force of the Cell Sb | Sb_2O_3, Solution || 3.5 *N* KCl, AgCl | Ag at 25° (Electrodes Nos. 3a, 4a and 5)

*P*H of soln.	Elect. Nos.	*E* (obs.), v.	*E*′ (*E*, corr. for j.p.), v.	E_{Sb} (*E*′ − 0.2061), v.	*E*″ (0.05915 *P*H), v.	E_0 (E_{Sb} − *E*″), v.	Dev. from E_0 = −0.1445, mv.	Dir. of app. to equilib.
1.018	5	0.1259	0.1220[a]	−0.0841	0.0602	−0.1443	−0.2	D
1.979	5	.1826	.1787	−0.0274	.1171	.1445	0.0	U
3.008	3a	.2391	.2388	+0.0327	.1779	.1452	+0.7	D
3.008	4a	.2395	.2392	.0331	.1779	.1448	+0.3	D
3.008	5	.2396	.2393	.0332	.1779	.1447	+0.2	D
3.008	5	.2384	.2381	.0320	.1779	.1459	+1.4	U
6.018	3a	.4149	.4144	.2083	.3560	.1477	+3.2	U
6.018	4a	.4170	.4165	.2104	.3560	.1456	+1.1	U
6.975	4a	.4731	.4727	.2666	.4126	.1460	+1.5	D
6.975	5	.4747	.4743	.2682	.4126	.1444	−0.1	D
9.905	3a	.6454	.6453	.4392	.5859	.1467	+2.2	D
9.905	4a	.6474	.6473	.4412	.5859	.1447	+0.2	D
9.905	5	.6461	.6460	.4399	.5859	.1460	+1.5	U
9.905	5	.6468	.6467	.4406	.5859	.1453	+0.8	D
11.14	5	.716	.716	.510	.6588	.1488	+4.3	U
12.561[b]	5	.8032	.8032	.5971	.7430	.1459	+1.4	D
12.889[c]	3a	.8225	.8225	.6164	.7624	.1460	+1.5	U
12.889	4a	.8224	.8224	.6163	.7624	.1461	+1.6	U

[a] The correction of 3.9 mv. for the liquid junction potential in this case was derived from measurements, to be published soon, on silver–silver chloride electrodes using 0.1 *M* HCl, 0.1 KCl and 3.5 *N* KCl solutions.

[b] The *P*H of this sodium hydroxide solution (0.05979 *M*) was calculated from hydrogen electrode measurements on the basis of no liquid junction potential correction.

[c] This value for 0.1330 *M* sodium hydroxide was derived from the preceding one using activity coefficients for hydroxide ion calculated from activity coefficients of potassium chloride and hydroxide given by Scatchard, This Journal, **47**, 648 (1925), from the molalities of the two solutions, and on the assumption of equal junction potentials in the two cases: $\Delta P_H = \log (0.1330 \times 0.776)/(0.05979 \times 0.811) = 0.328$.

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[33] Tank nitrogen was used, purified by passing over hot copper (prepared by reducing the oxide with hydrogen) and washing with strong sodium hydroxide solution, pure water and, finally, a portion of the same solution contained in the electrodes.

hours later the operation was repeated and in most cases the reading was the same as before. If not, this procedure was repeated until two consecutive readings checked within 0.2 mv. The potentials always rose with rinsing and standing. Later on in the work Electrode No. 5 was made up, differing from No. 4a only in that the cubic oxide was prepared from material obtained from the trichloride by water hydrolysis alone and heated in the presence of metallic antimony at 500°. This was to obviate any contamination from sodium salts used in the hydrolysis of the trichloride by the other method, or from pentavalent antimony. The final values in every case are listed in Table IV. After several readings of this series had been taken, it was apparent that, on the basis of the temperature corrections to the buffers which we were able to glean from the literature, the slope would still be slightly less than the theoretical from *P*H 3 to *P*H 10. The last possibility previously mentioned, that the reported temperature coefficients of the buffers are not correct, seemed the only explanation of this deviation. The simplest solution to this problem was to measure directly the difference in potential between the antimony–antimony trioxide electrode and a hydrogen electrode immersed in solutions of the same acidity.

The Measured Electromotive Force of the Cell Pt, H_2 | Solution Sb_2O_3 | Sb at 25°

In determining E_0 directly, the general procedure was to measure electrode No. 4a or 5 (the preceding solution always having been more alkaline) against the reference electrode for a period of two to three days until the potential had definitely become constant. The hydrogen electrode vessel was then filled with a portion of the same solution which had been used in filling the antimony electrode, and hydrogen was passed through for at least two hours before any measurement was taken. Junction was made in the following manner. The outlet cock on the antimony electrode was closed and a slight excess pressure of nitrogen allowed to develop; the cock on the intake side was closed, the nitrogen supply disconnected and the cock opened slowly, allowing solution to fill the intake tube to the orifice; the volume of solution escaping was sufficient to decrease the pressure inside the bulb enough to balance the hydrostatic pressure of the solution. A short length of carefully cleaned rubber tubing was attached to the hydrogen electrode vessel and filled with solution from the reservoir of this vessel; this was slipped over the intake tube of the antimony electrode making contact; the two cocks on the hydrogen electrode vessel were now opened for the reading, the hydrogen still bubbling. No change in level of the electrolyte on the hydrogen electrode took place, due to the hydrostatic balance previously set up in the antimony electrode.

After the reading had been taken, the electrodes were disconnected and the nitrogen supply reattached to the antimony electrode. From two to four hours later another reading was taken. In two instances the procedure was repeated the following day. Barometric readings were taken coincident with all measurements and the potentials were corrected to 1 standard atmosphere partial pressure of hydrogen at 25°. The maximum deviation from the mean of the two or four corrected readings was 0.16 mv. The measurements are presented in Table V. These results clearly indicate that any previous apparent departure from the theoretical slope was due entirely to errors in the reported temperature coefficients of the buffers; therefore, hydrogen electrode measurements were made on buffers of *P*H 3, 6 (phthalate), 7, 8 (borate), and 10 of Clark and Lubs, Ringer's buffer of *P*H 11.29, and 0.05979 *M* sodium hydroxide solution directly against the reference electrode, using a flowing junction. The correct *P*H of these buffers at 25° was calculated (Table I, Col. 5) and used in the rest of the tables. In these calculations the Bjerrum extrapolations found by Clark and the value -0.3374_6 v. for the potential of the 0.1 *M* calomel electrode were used.

TABLE V

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL PT, H_2 | SOLUTION, Sb_2O_3 | SB AT 25°

Solution		*E* (obs.), v.		Dev. from mean, mv.
0.1000 *M* HCl		0.14436		−0.13
0.0100 *M* HCl		.14449		.00
C. and L. buffer, *P*H 7		.14436		− .13
C. and L. buffer, *P*H 10		.14474		+ .25
	Mean	.14449	Mean	.13

The results of Table IV may now be considered. The correct value of E_0 was taken as −0.1445 v., the directly determined result. The maximum deviation of the D values of electrodes Nos. 4a and 5, between *P*H 1 and 10, from this value for E_0, is 1.5 mv. and the mean deviation, 0.5 mv. *U* values are consistently lower than D by more than 1 mv., except in 0.01 *M* hydrochloric acid. This bears out the results of Table III with regard to the necessity of approaching equilibrium from the alkaline side for the best results.

Discussion of Results

Our results point definitely to the conclusion that the potential of the antimony-antimony trioxide electrode attains its maximum accuracy only provided that: the presence of any unstable solid phase in the system, notably orthorhombic antimony trioxide, is carefully avoided; dissolved oxygen is eliminated from the solution; and the equilibrium is approached from the alkaline side, a circumstance for which we are unable to offer an adequate explanation. Under these conditions the potential of the electrode is a linear function of the logarithm of the activity of hydrogen ion, with the theoretical slope, from *P*H 1 to 10. It seems conservative to claim a probable accuracy of less than 0.6 mv. or about 0.01 *P*H. This compares very favorably with the hydrogen electrode under ordinary conditions. Schuhmann's investigation of the molal electrode potential of antimony provides excellent evidence that our range of applicability may be extended on the acid side to *P*H 0 with at least some acids; our own measurements in the two most alkaline solutions indicate that the error at *P*H 13 is not more than 2 mv. and with careful pretreatment with a stronger sodium hydroxide solution it may be reduced to 0.5 mv.

Although our results prove that cubic antimony trioxide is the stable solid phase over the range in acidity in which precise activity measurements are ordinarily required, the question may be raised as to the probable extent of its region of stability. Van Bemmelen and other workers[34] have asserted that the stable solid phase in the presence of hydrochloric acid at any dilution contains chloride, but their claims are without adequate support. Lea and Wood[35] found that very finely divided Sb_2O_3 was slowly transformed into $Sb_4O_5Cl_2$ in 0.125 *N* HCl. However, their material is not comparable with our definitely crystalline oxide; accordingly, to make a direct test of the stability of cubic antimony trioxide, certain acid and alkali solutions were shaken with an excess of the trioxide and the final systems analyzed, with the following results.

Soln.	Concn. of soln. at invariant point at 25°	Soln.	Concn. of soln. at invariant point at 25°
HCl	Approx. 0.10 *M*	HNO_3	Above 1
H_3PO_4	Approx. 0.06	NaOH	Above 2
H_2SO_4	Approx. 1		

In the last three cases solutions of the concentrations stated produced no new solid phase detectable under the petrographic microscope and underwent no determinable change in concentration after shaking for four days. In the sulfuric acid solution, however, a small amount of a new solid phase was detected after a lapse of one month. The first two invariant points were determined by starting with solutions of different initial strengths, slightly above the concentrations stated, containing a large excess of both solid phases, and analyzing the solutions by titration at one-week intervals for three weeks. The change was very slow after the second week and the results given are very probably within 0.01 *M* of the true invariant concentration. Above 0.10 *M* HCl and 0.06 *M* H_3PO_4, therefore, antimony trioxide is not the stable solid phase and the

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[34] Van Bemmelen, Meerburg and Noodt, *Z. anorg. Chem.*, **33**, 272 (1903); Le Chatelier, *Compt. rend.*, **100**, 737 (1885).

[35] Lea and Wood, *J. Chem. Soc.*, **125**, 137 (1924).

antimony–antimony trioxide electrode cannot be subjected to such solutions for long periods of time without injury. However, in solutions as concentrated as 0.16 M HCl or 0.15 M H_3PO_4, initially containing the trioxide only, no new solid phase is formed in a week or more and the solutions undergo no change in concentration; therefore, solutions as strong as these may be safely used in the electrodes for short periods of time (three to four days). This was actually done in the case of hydrochloric acid and the electrode behaved perfectly normally afterward. We are not prepared to state positively that cubic antimony trioxide is stable in all moderately dilute acids; exceptional cases may exist but in any event there need be but little difficulty in their detection.

On comparing the several values for the difference in potential between a hydrogen and an antimony–antimony trioxide electrode in solutions of the same acidity, or E_0, it is interesting to observe that our value obtained with precipitated antimony trioxide checks that found by Schuhmann, who used oxide of the same character, to 1.2 mv., or within the limit of error of both investigations. Our final value, using cubic crystals of the trioxide, is 6.7 mv. more positive than this preliminary result, or -0.1445 v. The work of former authors who used massive metal electrodes is so uncertain and irregular that it provides no reasonable basis for comparison with our own and Schuhmann's.

The use of nitrogen as a gas phase for the antimony electrode has distinct disadvantages for its practical application. However, our results in air so closely approached those in nitrogen as regards the magnitude of the deviations from linearity that the former electrode may be safely recommended for general use, provided that the value of E_0 is fixed by means of two or more buffers in the range desired.

Although the necessity for the very careful preparation of the materials comprising the antimony trioxide electrode has been stressed, emphasis has not been laid on its superior permanency to the hydrogen electrode. With a reasonable amount of care there is no reason why it should not remain in service for an indefinite period, merely displacing one solution with another, with the proper precaution that each is more acid than its immediate predecessor. The electrode is undoubtedly slower than the hydrogen electrode in attaining actual equilibrium but the P_{H} calculated about thirty minutes after the solution has been introduced is normally within 0.1 P_{H} of the equilibrium value and, since the error is always on the acid side, the true P_{H} can probably be estimated to within 0.05 P_{H}. In order to attain an accuracy of the order of 0.01 P_{H} or greater, twenty-four hours may be required, as compared with two hours for the hydrogen electrode; however, the relative lack of attention demanded and the inert character of the electrode as regards its effect upon the acidity of the solution itself more than compensate for the required wait.

The Free Energy of Formation of Cubic Antimony Trioxide and the Free Energy Change for the Transformation: Sb_2O_3 (orthorhombic) ⟶ Sb_2O_3 (cubic) at 25°

If 0.1445 v. is accepted as the best mean value for the electromotive force of the cell Pt, H_2 | Solution, Sb_2O_3 (cubic) | Sb, the free energy change for the cell reaction $3H_2(g) + Sb_2O_3 \text{ (cubic)} \longrightarrow 2Sb + 3H_2O(l)$, ΔF_1, $= -6 \times 0.1445 \times (96{,}500/4.185) = -19{,}992 \pm 20$ cal. If the change in free energy for the reaction $3(H_2(g) + 1^1/_2O_2(g) \longrightarrow 3H_2O(l)$, ΔF_2, $= -169{,}680$ cal. (probable accuracy about 0.1%),[36] the free energy of formation at 25° of cubic antimony trioxide is equal to the difference $\Delta F_2 - \Delta F_1 = -149{,}690 \pm 200$ cal. This value is recommended in place of Schuhmann's −148,600 cal. because of the indefinite crystalline characteristics of his oxide.

The free energy change for the transformation of orthorhombic to cubic antimony trioxide may be calculated from the electromotive force of the cell Sb | Sb_2O_3 (orthorhombic), Solution, Sb_2O_3 (cubic) | Sb. For this purpose two electrodes similar to Nos. 3a and 4a were made up, using orthorhombic antimony trioxide which had been freshly prepared by fusing precipitated oxide in a platinum boat in an evacuated Pyrex tube and cooling quickly after solidification had taken place. Immediately after setting up, the electrodes were washed, filled with buffer, the nitrogen was turned on and the usual procedure followed. Readings against the same reference electrode as used previously were continued for twenty-four hours; constant potentials were not attained. The final values of the two electrodes containing the two buffers P_H 9.905 and P_H 3.008 were 0.6350 v. and 0.2255 v., respectively. The best values on these same buffers for cubic oxide were 0.6474 v. and 0.2395 v., giving differences of 12.4 mv. and 14.0 mv., respectively. The average value, 13.2 mv., is judged to be accurate to 10% on the basis of these measurements. The free energy change for the transformation Sb_2O_3 (orthorhombic) ⟶ Sb_2O_3 (cubic) at 25° is, therefore, equal to $-6 \times 23{,}059 \times 0.0132 = -1826$ cal., or -1800 ± 200 cal. We can claim this only as a minimum negative value since the work with the precipitated oxide showed that even if the oxide saturating the solutions is mainly orthorhombic, if a certain amount of cubic is present, the electrode tends to assume a potential between that characteristic of the cubic and of the orthorhombic. Thus the difference in E_0 of both Schuhmann's and our precipitated oxide electrodes and of our cubic oxide electrodes is only about half the measured electromotive force of the cell under consideration.

In conclusion, the authors wish to express their gratitude to Dr. John Johnston for the suggestions and help he has given in connection with this work.

[36] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 485.

Summary

1. The potential of the electrode Sb | Sb_2O_3, Solution has been shown to depend on three main factors: (a) the crystalline character of oxide used, (b) presence or absence of air in the electrolyte, (c) direction of approach to equilibrium; the best results are obtained with cubic oxide, air-free electrolyte, and by pretreatment with a solution more alkaline than the one being studied. Under these conditions, the potential is a linear function, with theoretical slope, of the P_H of the solution; the difference between it and a hydrogen electrode in a solution of the same acidity is 0.1445 v. ± 0.2 mv. at 25°.

2. Equal accuracy may be secured without the necessity of excluding air, provided that the electrode is standardized by the use of two or more solutions of known acidity. Such an electrode is superior to the hydrogen electrode in that once set up it requires little further attention, is permanent and may be readily used for solutions the acidity of which is affected either by hydrogen alone or by hydrogen in combination with platinum black. Hydrochloric acid (and probably hydrobromic and hydriodic acids) may not be used in the electrode in a concentration exceeding 0.16 *M*, phosphoric acid in a concentration not exceeding 0.15 *M* and sulfuric acid in a concentration not exceeding 1 *M*, due to the formation of new solid phases. Nitric acid and sodium hydroxide may be used up to 1 *M* and 2 *M*, respectively, and perhaps further.

3. Because the behavior of the antimony–antimony trioxide electrodes indicated that previously determined temperature coefficients applied to the Clark and Lubs buffers were somewhat in error, the P_H of certain of these solutions (the accepted standards at 20°) were measured at 25° with the hydrogen electrode (Table I, Col. 5).

4. Antimony trioxide formed by the hydrolysis of antimony trichloride has been demonstrated to consist chiefly of orthorhombic crystals; the transition temperature of antimony trioxide has been found to be 570 ± 10°, the cubic form being stable below this temperature.

5. The free energy of formation of cubic antimony trioxide at 25° was found to be $-149{,}690 \pm 200$ cal. and the free energy of transformation, Sb_2O_3 (orthorhombic) $\longrightarrow$ Sb_2O_3 (cubic), -1800 ± 200 cal.

6. The potential of the decimolal calomel electrode has been derived from two different sources and found to be -0.3341 v.

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