LXI.—*The Use of the Antimony–Antimonous Oxide Electrode in the Determination of the Concentration of Hydrogen Ions and in Potentiometric Titrations. The Prideaux–Ward Universal Buffer Mixture.*

By HUBERT THOMAS STANLEY BRITTON and ROBERT ANTHONY ROBINSON.

ALTHOUGH the hydrogen electrode is the ultimate standard to which all measurements of hydrogen-ion concentration are referred, other electrodes are frequently employed, either because of ease of manipulation or owing to the inapplicability of the hydrogen electrode in certain solutions. A familiar example is the quinhydrone electrode, which, however, is useless in alkaline solutions and also for certain acids (*e.g.*, sulphurous). In the former case, no satisfactory electrometric method exists, with the exception of the hydrogen electrode and possibly the glass electrode, the use of which is best restricted to solutions of $p_H < 10$. Several workers have shown that the antimony–antimonous oxide electrode may often be used for the detection of end-points in titrations, and the work of Kolthoff and Hartong (*Rec. trav. chim.*, 1925, **44**, 113), Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1928, **50**, 3125), and Shukov and Awsejewitch (*Z. Elektrochem.*, 1929, **35**, 349) suggests that it might, under proper conditions, be used to determine p_H values accurately; in fact, Roberts and Fenwick state that the p_H may be measured to within 0·1 unit from the voltages set up after ½ hour's standing, or to within 0·01 unit after 24 hours. Consideration of the *E.M.F.*'s of the cell $Sb,Sb_2O_3|solution|H_2$, extrapolated from the data corresponding to solutions of various p_H values obtained by the different workers, reveals that Roberts and Fenwick obtained values for the antimony electrode which were 0·1 volt less positive than those of Kolthoff and Hartong, who, incidentally, demonstrated that their measurements could also be used to determine p_H values. The former workers used antimony crystals that had been electro-deposited at high *C.D.* from a hydrofluoric acid solution of antimony trioxide, together with antimony oxide obtained by the slow hydrolysis of the trichloride, and they consider that the results of " former authors who used massive antimony are so uncertain and irregular " that they bear no comparison with those obtained by them. In the presence of air they state that the variations of the electrode are erratic during the first hour, and, moreover, emphasise that if maximum accuracy is desired any dissolved air must be removed from the solution. On the contrary, Francke and Willaman, using massive electrodes (*Ind. Eng. Chem.*, 1928, **20**, 87), conclude that " if partially closed electrode vessels are used, if the stirring is accomplished without unnecessary agitation, and if readings are taken within two minutes, the results will be entirely satisfactory."

Even if accurate results could be obtained by the method of Roberts and Fenwick, the long time required before reproducible results could be obtained would preclude the electrode from being of use in measuring p_H values throughout the course of a potentiometric titration. The work now described has therefore been done with the dual object of ascertaining the scope of the antimony electrode as a titrimetric indicator and the extent to which the *E.M.F.*'s may be accurately converted into p_H values. For this purpose, the published p_H values of the Prideaux–Ward universal buffer mixture (J., 1924, **125**, 426) have been confirmed and measured at a larger number of stages in the neutralisation, and then used to calibrate the antimony electrode. A series of titrations of acids and salts, some of which could not be titrated in the presence of the hydrogen or quinhydrone electrode, has been carried out with the antimony–antimonous oxide electrode, and the calibration curve employed to ascertain the p_H values at different stages of the neutralisation and to determine the dissociation constants of the acids involved. Comparison of the values so obtained with those derived by the standard methods shows that the electrode possesses a wide range of applicability and is capable of rapidly indicating prevailing p_H values with a moderately high degree of accuracy.

EXPERIMENTAL.

The Modified Universal Buffer Mixture.

In most of the previous attempts to calibrate the potentials of the antimony–antimony oxide electrode in terms of p_H values, the *E.M.F* of the cell

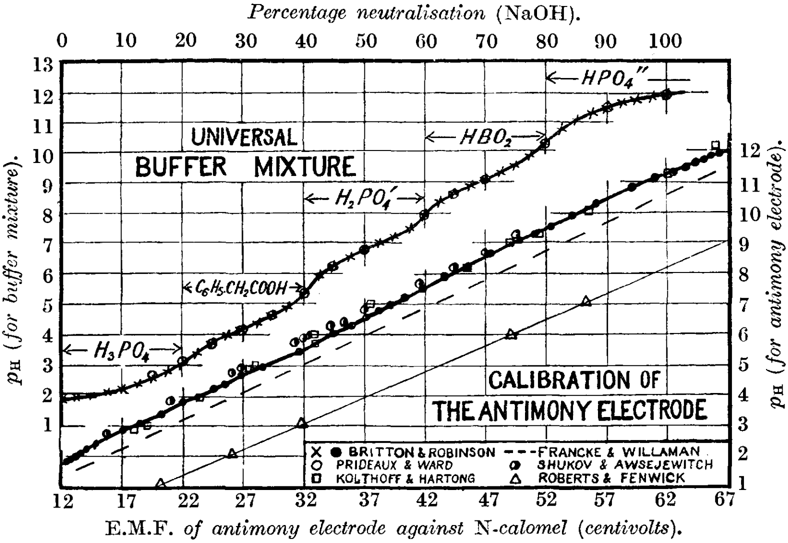
$Sb,Sb_2O_3|$Buffer solution of known $p_H|$Standard half element

was plotted against the p_H value. Erratic results were obtained by Kolthoff and Hartong with the electrode in solutions of p_H 5—7. Instead of using a series of separate buffer solutions, it was considered better to adopt a slightly modified form of the Prideaux–Ward universal buffer mixture, which, on gradual neutralisation with sodium hydroxide, would subject the electrode to continuous changes of hydrogen-ion concentration ranging from p_H 2 to 12. Moreover, the behaviour of the electrode could also be tested when it was immersed in the buffer mixture solution that had been previously neutralised to some desired stage. In this way it would be possible to ascertain whether the potential of the electrode could be considered as an indication of the true p_H values, not only during a titration, but also in the case of any single measurement.

Unfortunately, the p_H values, determined experimentally by Prideaux and Ward, corresponding to the successive stages of neutralisation, increase as a rule by amounts somewhat greater than 0·5 p_H unit, and in three instances by more than one p_H unit. As shown by one of the authors (Britton, " Hydrogen Ions," 1929, p. 188), the relationship between the p_H values and the degree of neutralisation is not strictly rectilinear, so that calculation by means of the interpolation formula advanced by Prideaux and Ward can only be expected to yield approximate results. In order, therefore, to use the universal buffer mixture as a suitable basis for the calibration of the antimony electrode, a considerable number of p_H values have been accurately measured over the whole range of neutralisation.

The universal buffer solution is composed of a mixture of phosphoric, phenylacetic, and boric acids, each 0·04*M*, neutralised with 0·2*N*-sodium hydroxide. Prideaux and Ward made a series of solutions by neutralising 100 c.c. of the mixture with the appropriate volume of alkali and diluting the solution to 200 c.c. In our experiments, we departed from this procedure in one respect, in that, instead of preparing a series of buffer mixtures, we titrated 100 c.c. of the acid solution with 0·2N-sodium hydroxide solution; the same solution, therefore, passed continuously through the whole range of p_H values from 2 to 12. This renders our data for the first 15% of the neutralisation hardly comparable with those of Prideaux and Ward, but as the small differences in concentration introduced have negligible effect on the acids involved in the remaining part, the data obtained by us should be in accord with the original values. The second col. of Table I gives the p_H values measured at 14° with the hydrogen electrode for every 2·5% neutralisation. These values were confirmed up to 70% neutralisation by using the quinhydrone electrode, the p_H value (9·1) then attained representing the limit to which this electrode could be used. In general, good agreement was obtained with the data of Prideaux and Ward, the only important divergence being at 35% neutralisation, where a difference of 0·15 p_H was observed.

FIG. 1.



The curve plotted in the upper part of Fig. 1, showing the relationship between the p_H values and the percentage neutralisation, emphasises the composite nature of the buffer solution, and on examination reveals that, if the linear equation of Prideaux and Ward be assumed to represent the entire curve, errors of as much as 0·2 p_H unit may occur at stages corresponding to the end of the neutralisation of one of the constituent acids and the beginning of the neutralisation of the next.

Preparation and Calibration of the Antimony Electrode.

Kolthoff and Hartong, and also Francke and Willaman, found that the change in *E.M.F.* of the cell $Sb,Sb_2O_3|Solution|Calomel$ per unit change in the p_H value of the solution was less than the theoretical, the latter workers finding that the equation $E = 0{\cdot}050 + 0{\cdot}054\ p_H$ holds at 25°. The data of the former investigators, however, would indicate that one linear equation is not sufficient to reproduce the change in *E.M.F.* between p_H 2 and 12, there being a discontinuity about p_H 6. In the first series of experiments, therefore, a number of different types of antimony and antimonous oxide preparations were used in the potentiometric titration of the buffer mixture with sodium hydroxide. In all cases, 100 c.c. of the solution were titrated with 0·2*N*-sodium hydroxide, the *E.M.F.* against the normal calomel electrode being measured after every addition of 2·5 c.c. of alkali. Saturated potassium chloride solution was used as the junction liquid. It was soon found that fairly vigorous stirring of the solution with a mechanically driven stirrer is essential; without this, it is impossible to obtain a steady reading on the potentiometer, the slightest current passing through the unstirred solution apparently setting up polarisation effects; indeed, an accidental stoppage of the stirrer was immediately reflected in a drifting of the potentiometer reading.

The first few titrations were made with two rods of pure cast antimony, supplied by Messrs. British Drug Houses Ltd., 4″ long, ¼″ diameter, dipping to about half their length in the solution. The rods had been previously oxidised on the surface by treatment with warm 50% nitric acid to form a layer of oxide (usually supposed to be the trioxide, but it was probably contaminated with appreciable quantities of the pentoxide, since the higher oxide is formed by repeated evaporation to dryness of the trioxide with nitric acid). Although on immersion in the solution the electrodes exhibited large changes in *E.M.F.*, this drift rapidly diminished and after 5 minutes, when the titration was begun, they gave reasonably steady values. Readings were then taken at every 2·5 c.c. about 3 minutes after the alkali addition. During this period no variation greater than 1 mv. was noticed. The two electrodes gave *E.M.F.*'s within 1 mv. of one another, and the results recorded in this titration were in remarkably good agreement with the *E.M.F.*'s which were finally considered correct. Oxidation of the metal surface with nitric acid, however, was abandoned, for it was found that (*a*) electrodes after standing over-night in distilled water did not give reproducible *E.M.F.*'s in the buffer mixture, and (*b*) subsequent oxide films produced by re-oxidation, after cleaning with emery paper, led to erratic results.

In the next series of experiments the same electrodes were used, but they were cleaned with emery paper at the beginning of each titration, giving a smooth bright surface, apparently free from oxide. Purified antimonous oxide was added to the buffer mixture. This oxide was prepared by the method described by Schuhmann (*J. Amer. Chem. Soc.*, 1924, **46**, 52), by precipitating basic antimonous chloride from a hydrochloric acid solution, redissolving it in acid, and reprecipitating the oxide by stirring the solution into a boiling sodium carbonate solution. The results of this titration were very satisfactory, steady *E.M.F.*'s being recorded which never deviated by more than 2 mv. from those registered in the first titration.

After 100 c.c. of 0·2*N*-alkali had been added to 100 c.c. of the buffer mixture, it was titrated back again with 0·2*N*-hydrochloric acid, potential readings being taken after each addition of 2·5 c.c. of acid. These readings corresponded exactly with those recorded in the previous alkali titration, except, of course, in the region where the first dissociation of phosphoric acid comes into play, *i.e.*, during the addition of the first 15 c.c. of alkali and the last 15 c.c. of acid, where dilution effects are noticeable. This agreement on reverse titration is of importance in that it shows that the *E.M.F.*'s are reproducible whether the equilibrium is approached from the acid or from the alkaline side.

By using similar electrodes but without the addition of oxide to the solution, excellent agreement with the previous data was obtained over nearly the whole range of p_H values, although deviations of about 4 mv. were observed at one portion of the titration over about 20 c.c. of alkali. This observation is in agreement with the work of Uhl and Kestranek (*Monatsh.*, 1923, **44**, 29), who found that good " breaks " could be obtained in the titration of acids against the antimony electrode without the addition of oxide, but it is, nevertheless, surprising that the metal contains sufficient oxide to give stable *E.M.F.*'s identical with those registered on the addition of oxide to the solution. Although in further titrations small quantities of oxide were added to the solution, it is apparent that in titrimetric work, where only the end-point of a reaction is to be measured, this addition is not necessary.

We have repeated this titration of the buffer mixture more than twelve times, using clean antimony bars and purified antimony oxide, and generally the *E.M.F.*'s have been concordant to within 2 mv. These titrations have been made several times with the original pair of electrodes, which had in the meanwhile been used in the titration of such acids as chromic and telluric. A new pair of pure antimony electrodes gave the same results and a specimen of "technical" antimony gave equally good agreement. Through the courtesy of Messrs. Locke, Lancaster and W. W. and R. Johnson and Sons, Ltd., of Millwall, we have been provided with specimens of cast antimony containing 5% of bismuth, lead, and tin respectively. Titrations of the buffer mixture were carried out with these alloys, and considerable differences were found between the *E.M.F.*'s of the cells containing alloy and those containing pure antimony. On an average taken over the p_H range 2—12, the 5% bismuth alloy gave *E.M.F.*'s 13 mv. lower than those of the pure antimony electrode, the deviation varying from 2 to 30 mv. On the other hand, the lead and tin alloys gave higher potentials than the pure antimony, the average deviations being 6 and 7 mv. respectively, and their ranges being 1—13 mv. and 1—15 mv. respectively.

A few experiments were performed in which electro-deposited antimony was used as electrode. Shukov and Awsejewitch deposited antimony from a 25% acetone solution of its trichloride on mercury-coated platinum wire 1 cm. long with a current of 0·6—2·2 milliamp. for 30 mins. They state that against the normal calomel electrode this electrode gives potentials related to the p_H of the solution by $E = 0{\cdot}009 + 0{\cdot}053\ p_H$ between p_H 2·78 and 9·19 at 14°. In the titration of the buffer mixture, we obtained steady *E.M.F.*'s that were in good agreement with those recorded by Shukov and Awsejewitch, the *E.M.F.* of the cell $Sb,Sb_2O_3|Solution|Calomel$ being raised by about 10 mv. by the substitution of electro-deposited antimony for bar antimony. Further preparations of these electrodes, however, failed to give results in such good agreement, for the difference between the cells containing the two types of antimony was in some cases as much as 30 mv. On continued use, the Shukov and Awsejewitch electrode deviates from their equation.

We have also prepared electrodes of the type described by Roberts and Fenwick, due originally to Cohen, Collins, and Strengers (*Z. physikal. Chem.*, 1905, **50**, 307); these consist of antimony deposited from hydrofluoric acid solution at a high *C.D.* at a platinum cathode and detached by gentle tapping of the cathode. A titration of the buffer mixture was carried out with this electrode, and also the variation of the potential of the electrode was measured during 24 hours while it was immersed in solutions of p_H 1·81 and 11·94. Admittedly we have taken no precautions to exclude air from our solutions, but we found it extremely difficult, and even impossible, to obtain trustworthy results. For example, in a titration of the buffer mixture we observed that the cell $Sb(electrolytic),Sb_2O_3|Solution|Calomel$ gave a voltage higher than the corresponding cell with a bar electrode by 64 mv. at the commencement of the titration. During the titration the difference became smaller, the two types of electrode being in approximate agreement at 35% neutralisation, after which the electrolytic antimony electrode gave lower *E.M.F.*'s, its behaviour being most erratic. When the two types of electrode were then immersed in a solution of p_H 1·81, the initial *E.M.F.* of the bar antimony sank from 0·127 to 0·121 after 12 hours, and to 0·115 after 24 hours, the corresponding *E.M.F.*'s of the electrolytic antimony being 0·284, 0·221, and 0·209.

The two electrodes were then immersed in a solution of p_H 11·94, the cell containing the bar antimony varying from 0·665 to 0·656 in 24 hours. In this case the electrolytic antimony gave an initial potential of 0·232, rising slowly to 0·353 after an hour and to 0·684 after 24 hours. In these two solutions, the *E.M.F.*'s observed by Roberts and Fenwick become, after correction for the difference in potential between the silver–silver chloride half-element which they used and the normal calomel, 0·239 and 0·835 volt respectively. This type of electrode is therefore quite unsuitable for use either in titrimetric work or for the rapid determination of p_H values.

We followed the drift in *E.M.F.* to which the bar electrode is liable for several hours in solutions of different p_H value. The variation was appreciable during the first few minutes after the introduction of the electrode, but after 5 minutes the *E.M.F.* usually became steady for several minutes; nevertheless during an hour, it showed an average drift of 4 mv. per hour taken over the 17 solutions of p_H value between 2 and 12 which have been studied. In all cases, however, the *E.M.F.* read 5 minutes after immersion of the electrode is reproducible and agrees with that recorded in a solution of the same p_H value obtained by direct titration of the buffer from either the acid or the alkaline side.

As a result of these experiments, we concluded that in cases where the antimony electrode can be used in the determination of p_H values with a moderate degree of rapidity, a bar of cast antimony is preferable to the electro-deposited form, and is trustworthy and simple in use. A calibration curve was therefore constructed by taking the mean of all the concordant, reproducible *E.M.F.*'s which had been obtained in the titration of the buffer mixture against a clean antimony bar in a solution containing suspended antimonous oxide. The means of these *E.M.F.*'s, E_{Sb}, are given in Table I, the voltages referring to the cell $Sb,Sb_2O_3|$Solution$|$*N*-Calomel, while in the fourth column are given the calculated *E.M.F.*'s, E_H, of the cell $H_2|$Solution$|$*N*-Calomel. The difference between these two *E.M.F.*'s, given in the last column, is that of the cell $H_2|$Solution$|Sb_2O_3,Sb$ at different p_H values of the solution.

The p_H of the solution is plotted against the *E.M.F.* of the antimony electrode in the lower part of Fig. 1. (The p_H co-ordinates

TABLE I.

Titration of 100 c.c. *of the buffer mixture with* 0·2N-NaOH *at* 14° *by means of the antimony electrode.*

C.c.	p_H.	E_{Sb}.	E_H.	Diff.
0	1·81	0·124	0·387	0·263
2·5	1·91	0·127	0·393	0·266
5	1·98	0·131	0·397	0·266
7·5	2·10	0·135	0·404	0·269
10	2·21	0·141	0·410	0·269
12·5	2·38	0·147	0·420	0·273
15	2·55	0·156	0·429	0·273
17·5	2·84	0·167	0·446	0·279
20	3·05	0·184	0·458	0·274
22·5	3·38	0·203	0·477	0·274
25	3·75	0·221	0·498	0·277
27·5	3·92	0·233	0·507	0·274
30	4·22	0·244	0·525	0·281
32·5	4·33	0·255	0·531	0·276
35	4·65	0·268	0·549	0·281
37·5	4·92	0·286	0·564	0·278
40	5·43	0·316	0·594	0·278
42·5	6·02	0·343	0·627	0·284
45	6·33	0·359	0·645	0·286
47·5	6·59	0·371	0·660	0·289
50	6·79	0·382	0·671	0·289
52·5	6·99	0·393	0·682	0·289
55	7·24	0·404	0·697	0·293
57·5	7·51	0·418	0·712	0·294
60	7·95	0·435	0·737	0·302
62·5	8·35	0·456	0·760	0·304
65	8·68	0·473	0·779	0·306
67·5	8·90	0·487	0·791	0·304
70	9·10	0·497	0·803	0·306
72·5	9·36	0·510	0·818	0·308
75	9·58	0·524	0·830	0·306
77·5	9·93	0·539	0·850	0·311
80	10·33	0·559	0·873	0·310
82·5	10·81	0·589	0·900	0·311
85	11·12	0·610	0·918	0·308
87·5	11·35	0·624	0·930	0·306
90	11·47	0·634	0·938	0·304
92·5	11·64	0·643	0·947	0·304
95	11·75	0·650	0·954	0·304
97·5	11·84	0·656	0·959	0·303
100	11·94	0·663	0·965	0·302

referring to this curve are given on the right-hand side.) The curve is continuous but only approximately linear. Francke and Willaman's data (*loc. cit.*) when plotted give a straight line of approximately the same slope as our curve but about 0·6—0·7 p_H unit below it. The data of Kolthoff and Hartong are irregular but give points in agreement with our curve, and those of Shukov and Awsejewitch give points lying above our curve by about 0·3—0·4 p_H unit. The values of these investigators are also indicated on the graph.

It will be observed that, with the exception of the data of Roberts and Fenwick, which alone refer to *E.M.F.*'s measured after the lapse of 24 hours, the calibration data obtained after the initial steady *E.M.F.*'s had been indicated by the several investigators with massive antimony, and in the case of Shukov and Awsejewitch with electro-deposited antimony, lie close together in Fig. 1. We have shown that the probable impurities in the metal have some effect on the initial *E.M.F.*'s, and also that these voltages may vary somewhat, depending on the treatment of the solution, *e.g.*, the efficiency of stirring. As it is probable that the conditions adopted in the present work would be difficult to reproduce in every respect by another worker, a calibration curve of each fresh electrode should be made under the precise conditions in which it is to be used.

Potentiometric Titrations.

In order to investigate the use to which the antimony electrode may be put in titrimetric work and in the determination of p_H

values, titrations of solutions of acids and salts of widely different nature were made. The solutions employed are given in the first two columns of Table II. The normal calomel electrode was used in each titration as the standard half-element, the junction with the titration cell being made with a saturated solution of potassium chloride. The titration curves are given in Figs. 2—5, in which the p_H values, read from the calibration curve from the observed voltages, have been plotted against the number of equivalents of the titrant. For the purpose of comparison, the titration curve of the sulphite solution with hydrochloric acid is reversed, the titration actually having been made from the alkaline to the acid zone. To ascertain whether the observed *E.M.F.*'s throughout the titration would lead to p_K values in agreement with those found by the accepted methods, calculations were made from the p_H values indicated at the addition of each one-eighth equivalent of titrant. The third column of Table II gives the limits of the p_K values so calculated, whilst in the next two columns are given the mean values.

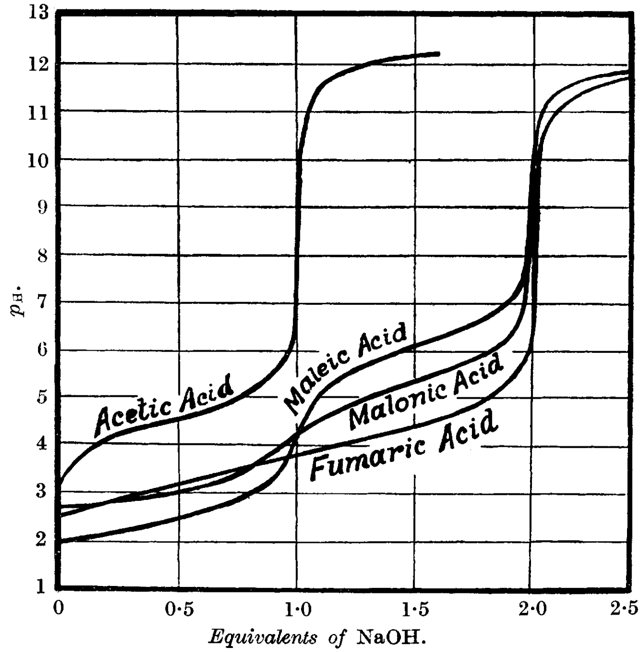
TABLE II.

			Mean.		Previous determinations.		
100 C.c. solution titrated.	Titrant.	p_K Range.	p_{K_1}.	p_{K_2}.	p_K.	Method.	Ref.
0·051*M*-Acetic acid	0·1945*N*-NaOH	4·52—4·65	4·58		4·73	—	
0·025*M*-Malonic acid	0·1945*N*-NaOH	2·77—3·14	2·99	—	2·70	*E.M.F.*	1
					2·74	,,	2
		5·35—5·45		5·38	5·36	,,	1
					5·39	,,	2
0·025*M*-Maleic acid	0·1945*N*-NaOH	1·94—2·09	2·05		1·34	,,	2
		6·00—6·12		6·06	6·94	,,	2
					6·29	,,	3
0·0167*M*-Fumaric acid (150 c.c. used)	0·1945*N*-NaOH	2·87—3·03	2·98		2·99	Cond.	4
					2·55	*E.M.F.*	2
		4·30—4·53		4·40	4·32	,,	2
					4·49	,,	5
0·04*M*-$NaBO_2$ + 0·02*N*-NaOH	0·231*N*-HCl	9·05—9·20	9·13	—	9·20	—	
0·04*M*-KCN + 0·02*N*-NaOH	0·231*N*-HCl	9·55—9·65	9·60	—	9·41	Special	6
0·045*M*-K_2SO_3 + 0·045*N*-NaOH	0·231*N*-HCl	2·64—2·81	2·70		—	—	
		7·65—7·82		7·74	7·0	Indicators	7
0·025*M*-Selenious acid	0·208*N*-NaOH	8·25—8·43	—	8·34	8·05	*E.M.F.*	8
					8·05	Indicators	9
					7·29	Cond.	10
0·025*M*-Telluric acid	0·208*N*-NaOH	7·75—7·97	7·84		—	—	
		—		*ca.* 12·5	—	—	
0·0322*M*-K_2CrO_4 + 0·0322*N*-NaOH	0·231*N*-HCl	6·95—7·16		7·07	6·4	*E.M.F.*	11
0·0462*M*-Sodium azide	0·240*N*-HCl	4·90—5·00	4·97		4·74	Cond. catalysis	12
					4·59	Glass electrode	13
					5·10	Cond.	14
0·04*M*-H_3PO_4	0·200*N*-NaOH	1·94—2·09	2·01		2·03	*E.M.F.*	15
					1·96	Cond.	16
		6·88—6·95		6·92	6·85	*E.M.F.*	15
					6·71	Cond.	16
		11·79—11·93		11·85 (p_{K_3})	11·57	*E.M.F.*	16
					12·44	Cond.	16
					11·55	*E.M.F.*	17

[1] Britton, 1925. [2] Mizutani, 1925. [3] Larsson, 1924. [4] Reyer, 1923. [5] Larsson, 1922, 1926. [6] Harman & Worley, 1924. [7] Kolthoff, 1920. [8] German, this paper, p. 470. [9] Willcox & Prideaux, 1925. [10] Blanc, 1920. [11] Britton, 1924. [12] West, 1900. [13] Hughes, 1928. [14] Oliveri-Mandalà, 1916. [15] Britton, 1927. [16] Abbott & Bray, 1909. [17] Prideaux & Ward, 1924.

The curves in Fig. 2 for acetic and malonic acids compare very satisfactorily with those obtained with the hydrogen electrode, and the p_K values (Table II) reveal that the electrode behaves well in the presence of these acids. Maleic and fumaric acids, being unsaturated, cannot be titrated against the hydrogen electrode, but the curves in Fig. 2 and the fair agreement with the published, but discrepant, p_K values illustrate the appreciable difference between the two isomerides.

FIG. 2.

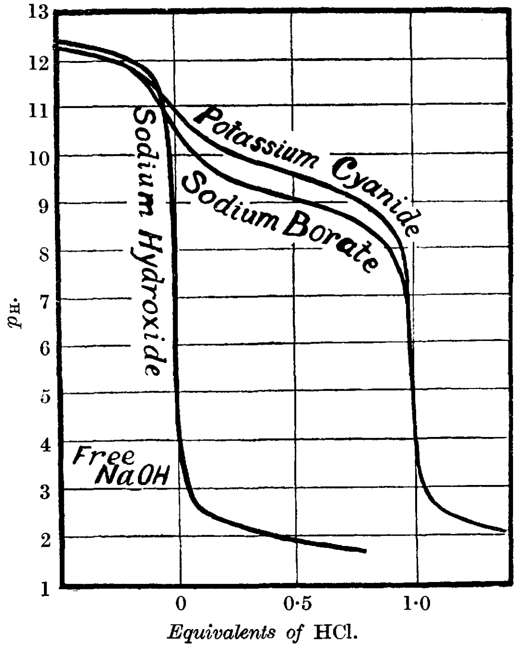


The data and curve for boric acid, Fig. 3, show that the electrode yields good results in feebly alkaline solutions.

No electrode has yet been found to be of use in the investigation of solutions of hydrocyanic acid. The antimony electrode gave steady *E.M.F.* readings, and the curve in Fig. 3 is throughout characteristic of that of a very weak monobasic acid.

The titration of the cyanide solution was carried out with Mr. E. N. Dodd, B.Sc., in connexion with work on complex cyanides, and this led to $p_K = 9{\cdot}60$, a value higher than those previously obtained. These, however, vary over such wide limits that comparison is not possible. The most recent value, $p_K = 9{\cdot}41$, obtained by Harman and Worley (*Trans. Faraday Soc.*, 1924, **20**, 502), is also higher than the earlier ones, and in the light of the work here described it is probably the most accurate. It has been confirmed by measuring the p_H values during the titration of potassium cyanide solution with hydrochloric acid by means of the usual comparator colorimetric method, and by the method of Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 165):

Fig. 3.



Determination of $p_{K_{HCN}}$ colorimetrically.

Fraction of KCN decomposed	0·125	0·25	0·375	0·50	0·625	0·75	0·875
p_H	10·34	9·98	9·55	9·30	9·00	8·80	8·50
p_K	9·49	9·50	9·33	9·30	9·22	9·28	9·35

Indicators used: Salicyl-yellow, Phenolphthalein, Thymol-blue, *m*-Cresol-purple.

Mean $p_K = 9·35$.

The remaining curve in Fig. 3 shows that the antimony electrode gives a sharp end-point in the titration of a solution of sodium hydroxide with hydrochloric acid, and, moreover, that the p_H values corresponding to the *E.M.F.*'s set up after the electrode had undergone a very large change were correct.

Fig. 4 corresponds to titrations of phosphoric acid and of the following acids which do not appear to have been investigated potentiometrically: sulphurous, selenious, selenic, and telluric. Neither the hydrogen, oxygen, nor quinhydrone electrode can be used in sulphurous acid solutions and, as Rosenheim and Krause (*Z. anorg. Chem.*, 1921, **118**, 178) have shown, the first is useless in selenious acid solutions owing to the deposition of metallic selenium upon the platinum black. Mr. W. L. German, M.Sc., in this laboratory has, however, titrated this acid in the presence of the quinhydrone electrode. His results are given in Table III.

TABLE III.

Quinhydrone titration of 50 *c.c. of* $0·049M\text{-}H_2SeO_3$ *with* $0·1N$-NaOH *at* 17°.

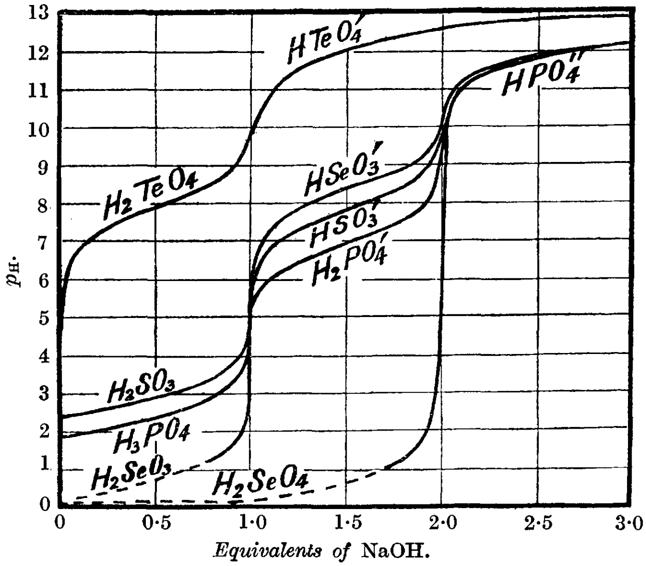
Fraction neutralised	0·125	0·25	0·375	0·50	0·625	0·75	0·875	Mean p_K.
			1st Stage of neutralisation.					
p_H	2·10	2·25	2·40	2·60	2·80	3·05	3·35	
p_{K_1}	2·47	2·48	2·68	2·49	2·50	2·50	2·45	2·51
			2nd Stage of neutralisation.					
p_H	7·30	7·70	7·90	8·05	8·25	8·45	8·74	
p_{K_2}	8·15	8·18	8·12	8·05	8·03	7·97	7·89	8·05

These figures compare well with $p_{K_1} = 2·40$ and $p_{K_2} = 8·05$ obtained by Willcox and Prideaux (J., 1925, **127**, 1543) by the indicator method and with $p_{K_1} = 2·31$ and 2·46 obtained by Rosenheim and Krause (*loc. cit.*) by the indicator and conductometric methods. Blanc (*J. Chim. physique*, 1920, **18**, 28), however, gives $p_{K_1} = 2·57$ and $p_{K_2} = 7·29$. The figure determined by means of the antimony electrode is $p_{K_2} = 8·34$. It proved impossible to determine the p_{K_1} value, for the *E.M.F.*'s registered during the first stage of neutralisation corresponded to p_H values below unity, indicating that in this region the antimony electrode was being involved in a reaction with the acid, thereby rendering the calibration inapplicable. These *E.M.F.*'s were quite steady, and the use of the electrode at this stage of the titration did not affect the *E.M.F.*'s later set up on further titration, since the p_K values determined for the second stage of dissociation were the same whether the free acid were titrated with alkali, or sodium selenite with hydrochloric acid. The titration curve for selenic acid shows a similar behaviour throughout the titration, for the *E.M.F.*'s recorded up to the end-point do not correspond to possible p_H values of the solution. Nevertheless, the antimony electrode can be used as an indicator of the end-point in the titration of this acid. The absence of any break at the point corresponding to the end of the first stage of dissociation indicates that selenic acid is a strong acid in agreement with the conductometric titration curve of this acid, which Miolati and Mascetti

(*Gazzetta*, 1901, **31**, i, 93) showed to have only one discontinuity at the point corresponding to complete neutralisation. Moreover, Ostwald ("Allgemeine Chemie," Leipzig, 1893) found that selenic and sulphuric acids have almost the same equivalent conductivities at all dilutions.

The p_H values prevailing throughout the first stage of neutralisation of telluric acid with sodium hydroxide led to a fairly constant value of p_{K_1}, *viz.*, 7·84. The values corresponding to the second stage, which are probably not very accurate, indicate that this stage of ionisation is that of an extremely weak acid, p_{K_2} being about 12·5.

FIG. 4.



These values cannot be considered as entirely satisfactory, for although the shape of the titration curve is reproducible, the actual voltages are not; *e.g.*, back-titration gave 7·38 for p_{K_1}. Nevertheless, both the curve and the approximate p_K values are of importance in that they establish the dibasicity of telluric acid, as opposed to its hexabasicity as required by the formula H_6TeO_6 suggested by Rosenheim and Weinheber (*Z. anorg. Chem.*, 1911, **69**, 261) and Gutbier (*ibid.*, 1901, **29**, 29). The conductivity data of the former workers can be brought into harmony with this view by taking 427 as a rough estimate of μ_∞ of H_2TeO_4 at 25°. In so doing, we have considered the ionisation, $H_2TeO_4 \rightleftharpoons H^\cdot + HTeO_4'$, and have assumed that the mobility of $HTeO_4'$ is equal to that of Cl'. Calculating from the conductivity data for the various dilutions, we obtain values of p_{K_1} of the order of 6. Though this value indicates that the constant, K_1, calculated from the titration curve is probably too small, it suffices to show, when coupled with the break obtained on neutralisation with 1 equiv. of alkali, that telluric acid is a dibasic acid whose first stage of ionisation is very weak. The extreme weakness of the ionisation of $HTeO_4'$, *viz.*, $p_{K_2} = $ *ca.* 12·5, shows that the tellurates of the alkali metals must be considerably hydrolysed, to extents of about 60%, thus : $K_2TeO_4 + H_2O = KHTeO_4 + KOH$.

The presence of free potassium hydroxide would explain the somewhat high values of the conductivity of potassium tellurate obtained by Gutbier. Moreover, this author stated that his cryoscopic data for telluric acid solutions supported the existence of H_6TeO_6 molecules in solution. The actual values of the molecular weights ranged from 201·4 to 228·7 (Calc. for H_6TeO_6 : 229·6) and compare almost as well with H_2TeO_4 (Calc. : 193·6), the ionisation being too small to have any appreciable effect on the freezing point.

The titration of potassium tellurite with hydrochloric acid was attempted, but a black deposit, probably of tellurium, was formed on the electrode and no steady *E.M.F.* readings could be obtained.

Although the antimony electrode can be used in the electrometric titration of sulphite solutions, yet the *E.M.F.*'s established during the second stage of the neutralisation of sulphurous acid show a definite drift.

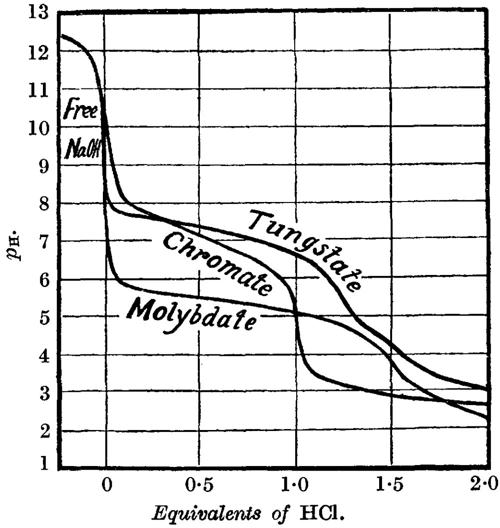
The phosphoric acid curve, Fig. 4, again demonstrates that the antimony electrode readily responds to considerable changes in p_H.

Fig. 5 illustrates the titration with hydrochloric acid of alkaline solutions of sodium chromate, tungstate, and molybdate. The first salt gave a steady *E.M.F.* during titration, but the p_{K_2} value calculated, *viz.*, 7·07, does not agree well with that previously measured (Britton, J., 1924, **125**, 1572). The titration of chromic acid with alkalis gave rise to the same type of result as was obtained with selenious and selenic acids in the acid region, the *E.M.F.*'s being much too small to correspond to the p_H of the solution, even if it were assumed that the acid were completely dissociated. Unlike those with the selenium acids, however, the *E.M.F.*'s registered in the case of chromic acid were by no means reproducible; indeed, in some cases the polarity of the cell was reversed. This erratic behaviour was reflected throughout the titration of this acid, the *E.M.F.*'s recorded in the second stage of neutralisation not being reproducible, and p_H values selected at stages in the course of any one titration did not give a constant value for p_{K_2}.

The results obtained in the acid titrations of sodium tungstate and sodium molybdate are of interest in that moderately good agreement was obtained with the results recorded by Britton and German (J., 1930, 1249, 2154), until a stage was reached in the acidification where the p_H was about 3. This is the point at which a " complex " has been shown to be formed, and after this stage very erratic results were obtained with the antimony electrodes.

Attempts to follow the titration of sodium orthovanadate with hydrochloric and acetic acids proved fruitless.

FIG. 5.



The antimony electrode has also been found applicable in the titration of sodium azide solutions with hydrochloric acid, and, as shown in Table II, indicates p_H values that are correct as far as can be judged from previous data.

The authors wish to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant which was made to assist an investigation out of which the present work has arisen, and also the Chemical Society for a grant from the Research Fund.

UNIVERSITY COLLEGE OF THE SOUTH-WEST,
EXETER.
[*Received, December 6th,* 1930.]